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Reverse Osmosis Field Test Treatment of Copper Cyanide Rinse Waters

American Electroplaters' Society, Inc, Winter Park, Fla

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Field tests of reverse osmosis (RO) were conducted on copper cyanide rinse waters at two different sites: Whyco Chromium Co. and New England Plating Co. At both sites, closed-loop treatment was used with plating chemicals recycled to the bath and purified water recycled to the rinsing operation. The objective of the tests was to establish, under actual plating conditions, the feasibility of RO treatment for copper cyanide plating wastes.

It was concluded that RO can be used to close the loop in copper cyanide plating. However, care must be taken to insure that adequate membrane life can be achieved. Where membrane life approaches that in traditional RO applications, the capital and operating costs for RO, compared to those for alternative treatment processes, are attractive. The cost attractiveness of RO depends on several factors specific for each installation. Bases for assessing capital costs, operating costs, and process credits are presented.

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REVERSE OSMOSIS FIELD TEST: TREATMENT OF COPPER CYANIDE RINSE WATERS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It was undertaken to demonstrate the effectiveness and economic feasibility of using reverse osmosis for closed-loop control of metal finishing rinse wastes under actual plant conditions. The reverse osmosis system concentrates the chemicals for return to the processing bath while purifying the wastewater for reuse in the rinsing operation. The results of the report are of value to R&D programs concerned with the treatment of wastewaters from various metal finishing, non-ferrous metal, steel, inorganic and other industries. Further information concerning the subject can be obtained by contacting the Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division.

David G. Stephan
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ABSTRACT

Field tests of reverse osmosis (RO) were conducted on copper cyanide rinse waters at two different sites: Whyco Chromium Co. and New England Plating Co. At both sites, closed-loop treatment was used with plating chemicals recycled to the bath and purified water recycled to the rinsing operation. The objective of the tests was to establish, under actual plating conditions, the feasibility of RO treatment for copper cyanide plating wastes.

At the first field-test site (Whyco Chromium Co.), both the flux and rejection of the membrane modules (duPont B-9 hollow fiber permeators) declined within a period sufficiently short to make RO unattractive on the basis of membrane replacement costs. The decline in performance is believed to be the result of chemical degradation of Reemay wrap material (used as a flow distributor within the permeator) as well as chemical degradation of the membrane itself. Supporting laboratory tests indicate that degradation of the Reemay component was related to exposure of the module to the brightener in the bath. Furthermore, in these laboratory tests the membrane appeared highly resistant to all major bath constituents, including the brightener; thus the constituent responsible for membrane attack during the field tests at Whyco Chromium Co. was not identified.

At the second field-test site (New England Plating Co.), the flux and rejection of the membranes were much more stable. As determined by NaCl solution performance tests, the flux did not decline significantly during 100 days of operating time. However, a moderate decline in NaCl rejection, from 90% to 85%, was observed over the same test period.

It is concluded that RO can be used to close the loop in copper cyanide plating. However, care must be taken to insure that adequate membrane life can be achieved. Where membrane life approaches that in traditional RO applications, the capital and operating costs for RO, compared to those for alternative treatment processes, are attractive. The cost attractiveness of RO will depend on several factors specific for each installation. Bases for assessing capital costs, operating costs, and process credits are presented.

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Mr. Roger Lisk and Mr. Jerry Wheelock were responsible for the day to day operation of the field test systems. This included obtaining all necessary data and samples, and performing maintenance and modifications required to keep the systems running properly.

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SECTION I

CONCLUSIONS

1. During field tests at Whyco Chromium Co., both the flux and rejection of the membrane modules declined within a period sufficiently short to make RO unattractive on the basis of membrane replacement costs.

   a. Tests on one of the field modules revealed that the decline in performance was the combined result of chemical degradation of the Reemay wrap-material/flow-distributor and chemical degradation of the membrane skin.

   b. Degradation of the Reemay component was simulated in the laboratory by exposure of a module to massive doses of brightener. For copper cyanide applications, the manufacturer should replace the Reemay component of the module with a more chemically inert material.

   c. During laboratory tests, the membrane itself was highly resistant to all major constituents of the bath including brightener; therefore, the constituent responsible for chemical degradation of the membrane skin during the Whyco Chromium Co. field test remains unidentified.

2. During field tests at New England Plating Co., the flux and rejection of the membrane module were much more stable. As determined by the standard NaCl solution performance tests, there was no substantial decrease in flux during the test period of 100 days. The NaCl rejection decreased from 90% to 85% during the same test period.

3. The economics of RO recovery of copper cyanide are closely tied to the membrane life which, at present, can be determined for each application only by field tests. For the specific field test at New England Plating Co., the net savings per day for RO recovery were insufficient to make the capital investment attractive on a purely economic basis (i.e., no positive return on investment). However, RO may still be the most attractive wastewater treatment alternative available, especially if zero discharge is required.

4. The dragout rate for most copper cyanide plating lines will greatly exceed the dragout rate observed during the field test at New England Plating Co. As the dragout rate increases, the credits resulting from closed-loop recovery increase. Provided these credits are not off-set by a shorter membrane life, the economic attractiveness of closed-loop recovery will increase with the dragout rate. The economics can become very attractive if, at higher dragout rates, the membrane life remains comparable to that observed at New England Plating Co.

SECTION II

RECOMMENDATIONS

1. In the light of the differences between the two field tests even though the bath compositions were similar, a plater should obtain some advance assurance from the membrane equipment supplier that the membrane module life will be adequate for his particular plating bath.

2. The design of a rinse system using RO recovery should be optimized for each installation. In the overall design, water conservation and efficient rinsing (e.g., countercurrent, spray, agitated, etc.) should be used to reduce the required capacity of the RO unit. The purity of the final rinse must be specified, based either on the allowable drag-in to a subsequent processing step or the appearance of the dried part. Means should be considered to control the rate of bath evaporation to give an optimum evaporation to drag-out ratio. The optimum ratio will be set by a balance between energy costs for bath evaporation and RO treatment costs.

3. It would be desirable to identify the cause of membrane deterioration in the Whyco Chromium Co. field tests in order to better define the limitations of RO for the treatment of copper cyanide plating wastes.

4. Field demonstrations of reverse osmosis should be extended to other baths. New membranes should be evaluated as they become available on a commercial or semi-commercial basis.

SECTION III

INTRODUCTION

Most platers recognize the need to reduce the amount of toxic substances discharged by the metal finishing industry. The basis for the extent of reduction which must be achieved by metal finishers is the Federal Effluent Guidelines for 1977[1], as well as receiving water standards. Moreover, the Federal Water Pollution Control Act Amendments of 1972 declare that it is the national goal to eliminate the discharge of pollutants into the navigable waters of the United States by 1985.

In the plating industry a major source of polluting effluent results from the discharge of spent rinse waters. The conservation of rinse water by countercurrent rinsing is always good practice, but in many cases countercurrent rinsing alone cannot eliminate rinse water effluent. In looking toward the national goal for 1985, increasing attention is being focused on closed-loop processes operating on the rinse water from a specific plating bath. These processes recover purified water that can be reused in rinsing and concentrated plating chemicals that can be recycled to the bath.

Reverse Osmosis (RO) can be used to recover plating chemicals and purified water from rinse water in a closed-loop system. The advantages and limitations of RO have been discussed previously[2,3]. As part of this program in-house pilot plant tests were conducted[2,3] to determine the feasibility of treating a variety of plating baths with the commercially available membranes. The results indicate that RO shows promise for the treatment of a number of plating bath rinse waters.

Before recommending that plating facilities purchase RO equipment, it is essential to demonstrate the capabilities of RO under realistic conditions. This can best be done by operating a full-size RO demonstration system in an actual plating shop. As part of an on-going program to investigate the applicability of RO to metal finishing waste treatment problems, field tests were conducted on copper cyanide plating baths at two different locations:

- Whyco Chromium Co., Thomaston, Conn.; and
- New England Plating Co., Worcester, Mass.

The objectives of the field tests were:

- --to obtain information on the potential limitations of closed-loop RO treatment;
- --to determine the performance (flux and rejection) of the RO modules, and the deterioration of performance with time; and
- --to assess the economics of the closed-loop RO recovery process.

Copper cyanide was selected for the RO field tests for the following reasons:

- --Cyanide wastes make a significant contribution to the plating waste problem.
- --Many plating shops contain copper cyanide baths.
- --The RO treatment of cyanide wastes has not been previously demonstrated.
- --Copper cyanide baths operate at elevated temperatures (~150°F) with significant bath evaporation. Auxiliary evaporation of the RO concentrate is not required before returning the concentrate to the bath.

The RO modules used in the field tests were duPont B-9 Permasep® Permeators which contain the polyamide membrane in hollow fine fiber configuration. The polyamide membrane is the only commercially available membrane material which can withstand the high pH of the cyanide solutions. The other commercially available membrane (cellulose acetate) is limited to a pH of 2.5 to 8.

Membrane performance was evaluated by measuring the flux and rejection as a function of operating time. The flux is defined as the rate at which permeate passes through a unit area of membrane surface under specified conditions. For the duPont modules, productivity (permeate flow rate per module) is reported rather than flux per se. The rejection is a measure of the degree to which dissolved substances are prevented from passing through the membrane. Rejection is defined by the equation:

$$\text{Rejection} = \frac{C_f - C_p}{C_f} \quad 100\%$$

where:

C_f = Concentration in the feed

C_p = Concentration in the permeate

SECTION IV

PHASE I: FIELD TESTS AT WHYCO AND RELATED INVESTIGATIONS

GENERAL

Field tests of RO for treatment of copper cyanide rinse waters were initiated at Whyco Chromium Co. The copper cyanide bath was part of a copper-nickel-chrome line used to plate a variety of die-cast parts. The plating bath was about 4,000 gal in size. It was preceded by a copper strike and followed by two rinses, an acid dip, and a final rinse. The RO system operated in conjunction with the two rinse tanks between the plating bath and the acid dip. The composition of the plating bath is shown in Table 1.

The plating line was an automatic rack line that was operated two shifts per day when the work load was heavy. However, during the period of the field tests, the copper line was operated on the average of one shift per day. After the RO system had been in operation for about 400 hours, the line was shut down for extensive modifications. Some additional data were obtained after the shut-down by operating the RO unit under "simulated" plating conditions. Plating was simulated by using a metering pump to transfer 40 gallons per day (estimated daily dragout for three operating shifts) from the bath into the first rinse and from the first rinse into the second rinse. The plating bath was maintained at its normal operating temperature (155°F) to simulate bath evaporation.

Because of the rapid deterioration in membrane performance observed in the Whyco field tests, a number of laboratory investigations were undertaken. The results of these investigations are reported in this section along with the field test results.

EXPERIMENTAL

Field Test System

A detailed process and instrument diagram of the unit is shown in Figure 1. The centrifugal booster pump (P1; Flotec Model C6P8) was used to withdraw about 5 gpm of feed from the first rinse and pass it through two one-

TABLE 1. COMPOSITION OF FIELD TEST COPPER CYANIDE BATHS

Whyco		New England Plating Co.	
$Na_2Cu(CN)_3$	16 oz/gal	$K_2Cu(CN)_3$	21 oz/gal
(Cu as metal	6 oz/gal)	(Cu as metal	6 oz/gal)
NaCN	2.5 oz/gal	K CN	3.5 oz/gal
Rochelle salts	4.0 oz/gal	Cuprolite 20*	6% vol.
Brightener**	2000 ppm vol.	Brightener**	2000 ppm vol.
pH	11-12	pH	13-13.5
Temp.	155°F	Temp.	140°F
Purification	Continuous active carbon filtration	Purification	Continuous active carbon filtration

* A Udylite Rochelle substitute

** MacDermid Cl o'ight Copper

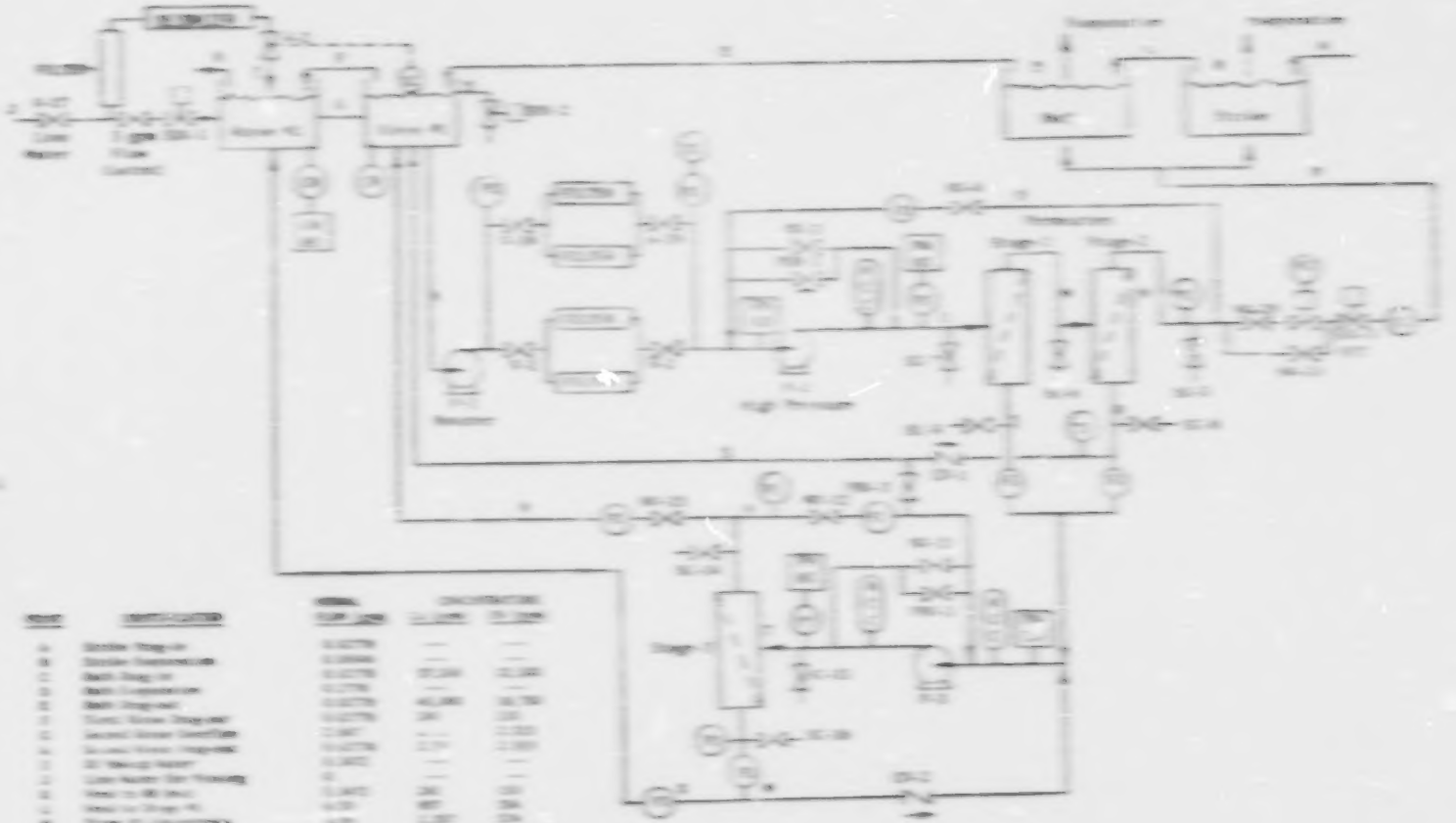


Figure 1. Process and Instrument Diagram for Alpha Field Test System.

micron cartridge filters (Filterite Model UTAW20U) in parallel. The pressure drop across the filters was measured (PI) to determine when cartridge replacement was necessary. A spare set of filters allowed cartridges to be changed without shutting the system down. The temperature was measured (TI) at the discharge from the filters.

A high pressure piston pump (P2: Cat Pump Corp. Model 01001) pressurized the feed to 300-400 psi. The discharge pressure was controlled by a needle valve (NV-3) in the pump by-pass. An accumulator on the pump discharge was used to dampen pressure pulsations. A high pressure switch and alarm (PA-HI) and a pressure relief valve (PRV) protected the RO modules from over-pressurization, and a low pressure switch and alarm (PA-LO) prevented the pump from running dry in case of fluid loss. The feed was passed through two RO modules (duPont B-9 Permasep Permeators Model 0440) in series. These modules are designated as "stage 1" and "stage 2". The total pressure drop across the modules was measured (PI). A portion of the concentrate was returned to the strike and/or bath, and the flow rate was maintained constant by the flow control valve (FC). The remainder of the concentrate was recycled to the suction of the high pressure pump. This recycle was required in order to maintain the recommended flow rate through the duPont modules.

The permeate from stages 1 and 2 was combined and repressurized by a second piston pump (P3: Cat Pump Corp. Model 00501) which was fitted with the same type of accumulator and high and low pressure safety devices as the pump for stages 1 and 2. The feed was passed through a third RO module, stage 3, which was identical to stages 1 and 2. The concentrate from stage 3 was returned to the first rinse and the permeate to the second rinse. A high-pressure overflow line (line "S") and a low-pressure recycle line (line "W") were included to keep the pump suction for stage 3 between 0 and 30 psi.

In addition to measuring the pressures (PI) and flows (FI) at various points in the RO unit, conductivity probes and a recorder (CR) were used to continuously monitor the rinse water quality. A conductivity alarm in the second rinse would shut down the RO system if the pre-selected conductivity set-point were exceeded. If the RO system were shut down, normal countercurrent rinsing

would resume automatically using a line-water flow of 3 gpm.

During closed-loop operation of the PD system the only non-plating loss of chemicals was by dragout from the second rinse; the only loss of water was by evaporation from the bath (and strike). Deionized water was used for make-up since the use of line water would introduce salts into the system which would be recovered and reqycled to the bath along with the plating chemicals. These could eventually build up to such an extent that plating quality would be adversely affected.

The calculated flow rates and concentrations of copper and cyanide are shown in Figure 1 for various points throughout the RO system and plating line. The assumptions upon which the calculations are based are given at the bottom of the tabular insert. The calculated copper concentration in the second rinse is about [illegible]. The advantage of reprocessing the permeate from stages 1 and 2 in a third RO stage is that lower concentrations can be maintained in the second rinse than for process designs which do not retreat the permeate. This advantage must be weighed against the increased cost and complexity of the "staged permeate" process.

The materials of construction used in fabrication of the system were 316 SS for high pressure lines and PVC and polyethylene for low pressure lines.

Laboratory Life-Test System

The flow schematic for the test system used in laboratory life tests is shown in Figure 2. Feed was withdrawn from the feed tank, pressurized by a positive displacement pump (Yarway Cyclophram Model 672), and fed to the RO module. An accumulator (ACC) was used to dampen pressure pulsations; a low pressure switch (LPS) protected the pump from running dry in case of fluid loss; and a high pressure switch protected the module from overpressurization. The feed pressure was measured (P), and the pressure was set by a back pressure regulator (BPR). The concentrate and permeate were combined and returned to the feed tank so that the feed concentration was time invariant. Heat was removed from the system by a cooling coil in the tank. During a portion of the life test copper was plated from a copper-plate anode (A) to a stainless-steel-pipe cathode (C).

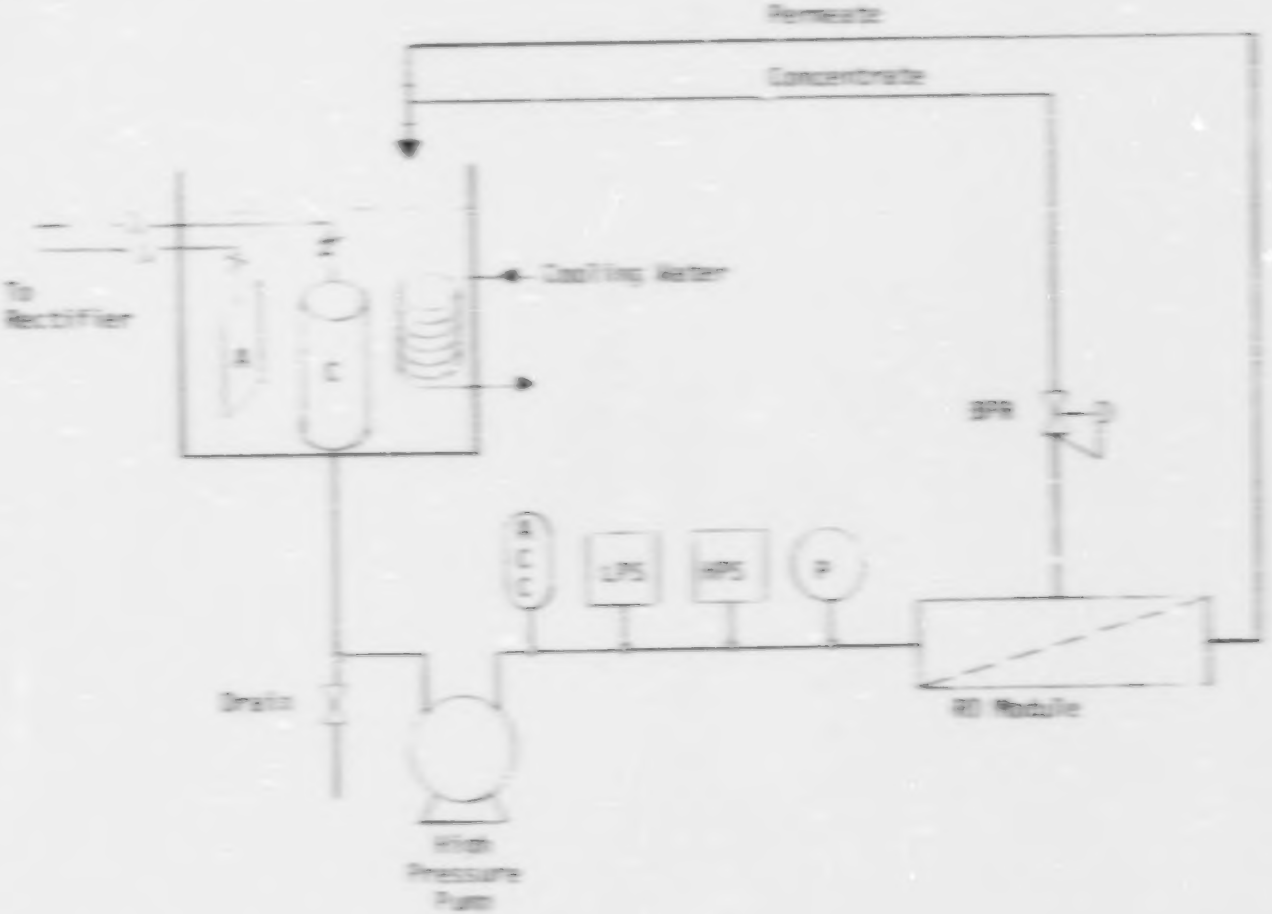


Figure 2. Flow Schematic for Laboratory Life Test System.

Samples were taken periodically for conductivity analyses. Feed samples were withdrawn from the feed tank; concentrate and permeate samples were withdrawn from the end of their respective return lines by removing them from the mixing tee. Flow rates were measured by the bucket-and-stopwatch technique.

In general, the feed solution was prepared at 20% of bath strength and the pH was adjusted to 11. The full-strength bath composition is:

CuCN	8.6 oz/gal
NaCN	11.3 oz/gal
Rochelle Salts	4.0 oz/gal
Brighteners	2000 ppm

Assays

The only assay performed on a regular basis during the field test was conductivity. Since the deterioration in membrane performance was so rapid, the expense of more complete analytical work did not appear justified. Several weekly samples were taken and analyzed for total dissolved solids (gravimetric technique), and the TDS results showed a close correspondence to the conductivity results.

For the laboratory life tests, conductivity was again the only analysis performed regularly. The conductivity was measured with a battery-operated conductivity meter that was calibrated with a NaCl standard.

RESULTS OF FIELD TEST

General Operation

The field demonstration unit was operated intermittently over a three-month period. During this time certain problems became evident. The most serious problem was a gradual deterioration in performance of the membrane modules which finally necessitated a temporary halt in the field test program. A few minor mechanical problems, associated with the staged permeate mode of

operation, were resolved during field testing and, mechanically, the unit operated satisfactorily.

Since the rinse water was treated in a closed loop, a build-up of temperature was anticipated. There were two sources of heat input: 1) heat was transmitted to the first rinse via parts and drag-in from the warm plating bath; and 2) heat was introduced in the RO unit where pumping energy was converted to frictional heat. There were also two sources of cooling: 1) heat transfer to the surroundings; and 2) addition of deionized water at a rate sufficient to compensate for bath evaporation. Although rinsing is more efficient at higher temperatures,the duPont modules are not recommended for use above 95°F. On very warm summer days the temperature of the feed to the RO system climbed above this limit. In applications where the ambient temperature can exceed the 95°F limit a heat exchanger should be installed on the feed to the RO unit with the cooling water thermostatically controlled. A separate cooling-water drain system is preferred so that the volume of waste going to the chemical treatment system is not needlessly increased with spent cooling water.

Deionized water was added to the final rinse at a rate of about one-third gallon per minute. Rapid exhaustion (15 days) of the exchange resins proved to be an annoying and costly maintenance problem. The regeneration frequency could be greatly reduced by pretreating the line water with RO before deionization, or perhaps by using RO alone.

Productivity (or Flux)

The productivity of a given module is the rate at which permeate is produced under specified conditions. The productivity is dependent on temperature, pressure, feed concentration, and conversion. The measured productivity was corrected to 400 psi and 77°F (normal operating conditions for the duPont module) using the duPont Technical Information Manual. However the data were not corrected for variations in feed concentration and conversion.

The conversion is the ratio of the permeate flow to the feed flow. For a module operated at near-zero conversion, the concentrations of the feed and concentrate streams are nearly the same. Thus the average concentration

on the feed/concentrate side of the membrane is very nearly the same as the feed concentration. On the other hand, a module operated at high conversion will produce a concentrate stream that is much higher in concentration than the feed stream. In this case, the average concentration on the feed/concentrate side of the membrane will be substantially greater than the feed concentration. For two modules operated at the same pressure, temperature, and feed concentration, the flux will be lower for the module operated at the higher conversion since flux decreases with increasing average concentration on the feed/concentrate side of the membrane.

The concentrate withdrawal from stage 2 was fixed at 1.50 gpm. The conversion for stage 2 is given by:

$$f_2 = \frac{P_2}{P_2 + 1.50}$$

where P_2 is the productivity (permeate flow rate) of stage 2. The conversion for stage 1 is given by:

$$f_1 = \frac{P_1}{P_1 + P_2 + 1.50}$$

The feed to stage 3 was maintained approximately constant at 5 gpm so that the conversion for stage 3 is given by:

$$f_3 = \frac{P_3}{5.0}$$

From these equations the conversion for stage 1 decreases from 41% to 33%, for stage 2 from 65% to 53%, and for stage 3 from 64% to 40% as the operating time increased (i.e., as flux decreased).

The feed concentrations to the RO modules were not fixed and could vary greatly depending on the amount of work passing through the rinse. The uncontrolled feed concentration is a much greater source of error than the rather small variations in conversion.

The productivities of the three modules are given as a function of operating time in Table 2, and corrected productivities are plotted in Figure 3. The "operating time" gives the cumulative hours during which the RO unit was running, as opposed to "exposure time" which is the cumulative time during which the modules were in contact with the feed solution.

Over the first 400 hours (normal operation) the flux declined rather rapidly with time but the decline seemed to taper off and approach a plateau value. The decline was the greatest for stage 2 which was exposed to the most concentrated feed solution and was the least for stage 3 which was exposed to the most dilute solution. The flux for stage 2 declined to 60% of the initial flux after only 300 hours (12.5 days) of operation. At 300 hours a new module was installed in stage 2, and the flux began to drop as before.

During simulated operation (metering pumps used to simulate dragout from the bath and first rinse) the drop in flux was much more rapid than during normal operation. It is quite likely that the simulated dragout rate was higher than the average normal dragout rate. If the curves for simulated operation are extrapolated, the predicted fluxes at 750 hours (1 month) will be about one third their initial values.

The drop in flux is much too large to be explained in terms of compaction of the fibers. The other possibilities include plugging by particulates in the feed, plugging by precipitation of a sparingly soluble salt during concentration, and chemical attack by some constituent in the feed. Of these possibilities the latter is the most likely. Destructive tests on the stage 2 module showed no sign of plugging or fouling.

Rejection

The rejection measures the degree to which plating salts are prevented from passing through the membrane. The rejection based on feed concentration ($r = 100\,[C_f - C_p]/C_f$) depends on the operating pressure, the conversion, and the feed concentration. The operating pressures and conversions were reasonably constant for the three modules so that only minor corrections

TABLE 2. FLUX AND PRESSURE AS A FUNCTION OF OPERATING TIME

Operating Time (hrs)	Temp. (°F)	Pressure (psi)[a]			Flux (gpd)			Corrected Flux (gpd)[b]		
		Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3
2	70	400	385	375	2.50	2.25	2.52	2.94	2.79	3.74
4	74	395	380	370	2.75	2.40	2.60	3.06	2.70	3.76
22	68	375	380	375	2.55	2.40	2.50	2.66	2.74	3.16
85	84	375	357	298	2.55	2.10	2.48	2.45	2.73	3.16
88	86	360	345	292	2.57	2.70	2.58	2.43	2.86	3.86
244	94	355	340	265	2.50	1.95	2.70	2.18	1.76	3.20
300	77	380	365	325	1.76	1.60	2.15	1.85	1.75	2.65
340	90	378	365	300	2.25	2.65	2.78	2.38	2.69*	2.80
400	90	375	355	325	2.15	2.10	2.40	2.19	2.26*	2.60
416	62	340	375	350	1.50	1.50	1.75	2.27	2.49*	2.60
440	63	340	375	350	1.40	1.50	1.75	2.12	2.43*	2.60
488	81	375	345	300	1.90	1.90	2.00	1.91	2.01*	2.51
540	70	350	338	375	1.40	1.40	1.65	1.60	1.67*	1.98
560	70	350	325	350	1.30	1.40	1.65	1.67	1.54*	2.10

a) Pressure measured at feed. For Stage 2 feed pressure was determined by dividing the ΔP equally between Stages 1 and 2.

b) Flux corrected to 400 psi and 77°F using duPont correction factors from Technical Information Manual.

* A new module was installed in Stage 2 at 300 hours operating time.

Figure 3. Corrected Productivity vs. Operating Time (Wkycm).

for variation in pressure and conversion would be anticipated. However, the feed concentration to a given module varied significantly depending on the amount of work passing through the rinse. The variability of the feed concentration represents the largest source of error in the data. It is not possible to conveniently correct the data to a fixed feed concentration as will be discussed in the following section. Therefore no correction factors were applied to the rejection data.

The conductivity rejection of plating salts is given as a function of operating time in Table 3 which also gives the conductivity and (in some cases) pH of the feed to each stage. The conductivity rejections are plotted as a function of operating time in Figure 4.

There are several interesting trends in this rejection data. The obvious trend is the rapid decrease in rejection for stages 1 and 2. During a total operating time of about 23 days, three good modules were consumed. At a replacement cost of $1206.00 this represents an unacceptable operating expense. The overall rate at which the rejection decreases is greater for stage 2 suggesting that the greater decrease is related to the higher feed concentration for stage 2.

During simulated operation (after 416 hours) the rejection for stages 1 and 2 decreased at a significantly greater rate. At 560 hours the rejection of stage 1 had dropped to 28%, and stage 2, to 21%. At this point the conductivity alarm in the second rinse was triggered and the entire RO unit was automatically shut down. The second rinse alarm was set at about 500 μ mhos/cm which is three times the conductivity of line water used for normal counter-current rinsing. At this point it was decided to terminate the field tests until the cause for the decrease in rejection could be determined.

One of the most significant features of Figure 4 is that the rejection for Stage 3 remains substantially constant over the entire test period. This cannot be entirely attributed to the lower concentration in stage 3 since, as shown in Table 3, the feeds to stage 3 and stage 1 are not really that much different in terms of conductivity. The high constant rejection for stage 3 indicates that the constituent responsible for the decrease in rejection does not pass through the membrane of stages 1 and 2 even though their rejections are low.

[illegible]

[illegible]

[illegible]

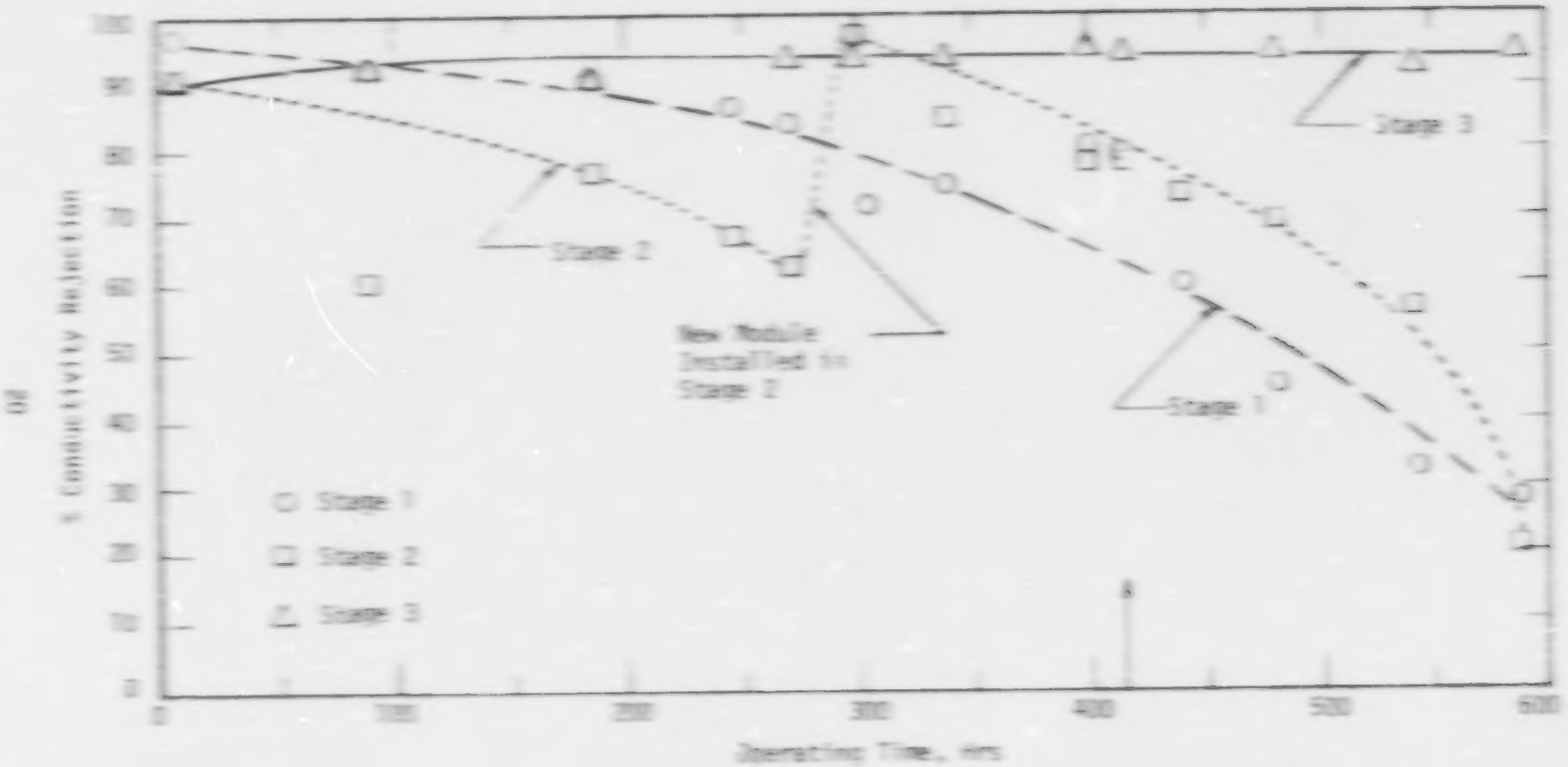


Figure 4. Conductivity Rejection of Plating Salts vs. Operating Time (Whyco).

INVESTIGATIVE TESTS ON FIELD MODULE

When the original stage 2 module was removed after 300 hours of operation its conductivity rejection for plating chemicals had dropped to 60%. Several cleaning procedures were performed for the removal of common foulants, but no improvement in rejection was obtained. During the cleaning procedures the NaCl rejection of the module was measured under standardized conditions (400psi, 77°F, 75% conversion, 1500 ppm feed). The measured rejections were 58% and 60% as compared to 90% for a new module. This confirms that significant damage did occur in the field.

The module was returned to duPont for more extensive tests. The duPont tests involved opening the fiber bundle, visually inspecting the various internal components, and making physical tests on the fibers. These tests resulted in the following findings:

1. There was no evidence of mechanical defects.
2. There was no evidence of any scaling, particulates, or foulants in the fiber bundle.
3. There was no significant deterioration in tensile properties or collapse resistance of the fibers.
4. The Reemay spacer (which functions as a flow distributor in the fiber bundle) showed significant deterioration in physical properties.
5. Permeation tests, conducted by making a mini-permeator from about 150 of the fibers in the module, showed high salt passage caused by severe skin damage.

These results indicate that the decrease in rejection was caused by a chemical attack of the membrane fiber rather than by particulate plugging, precipitation, or deposition of foulants on the membrane surface. The decrease cannot be attributed to direct hydrolysis at high pH since the upper pH limit of 11 was not exceeded. In addition, the rejection for stage 3 did not decrease even though the pH of the feed to stage 3 was nearly the same as for stages 1 and 2 (see Table 1).

LIFE TESTS ON FULL-SIZE PERMEATOR

If direct attack by OH^- is ruled out, there must be some other constitutent of the bath which was responsible for the rejection decline. The constituents of the Whyco bath are: copper cyanide, sodium cyanide, sodium hydroxide, Rochelle salts, and a selenium-based brightener (MacDermid CI Bright Copper[III]). None of the major constituents of the bath appeared to be likely candidates for attacking the membrane. Previous life tests with other cyanide solutions showed that the membrane has good cyanide resistance. Copper is also an unlikely candidate and in any case could not be removed from the bath. Sodium hydroxide can be easily handled provided a pH of 11 is not exceeded. Aside from the possibility that some impurity in the bath was responsible for the decline in rejection, the selenium brightener, which contains an inorganic oxidizing agent, appeared to be the most reasonable choice as the attacking constituent. Since chlorine, also an inorganic oxidizing agent, is known to chemically attack the membrane, the oxidizing agent in the brightener could conceivably exhibit similar behavior. It is anticipated that all selenium-based brighteners would behave in essentially the same way, so the problem would not be specific to the particular brand of selenium brightener used.

Laboratory life tests were conducted to determine what effect the brightener had on membrane performance. The laboratory life test system (total recycle) was described previously. One of the limitations encountered in using a total-recycle system is that a foulant in the feed tank can interact with the membrane in several passes through the module and thus be removed from the system. The only observed effect is a very slight (usually undetectable) drop in membrane performance. In an actual system the membrane is continually exposed to the foulant resulting in a gradual decline in performance. Thus in a total-recycle system it is necessary to ensure that the membrane receives the same total exposure to the foulant as would be received in an actual system.

Life tests were conducted with three different feed solutions: a synthetic solution of plating bath chemicals at 20% of bath concentration but without the brightener; the same solution with a considerable excess of brightener added at various times to simulate a continuous input of brightener; and the actual plating bath solution (with the recommended concentration of brightener but with no excess added) diluted to 17% of bath strength.

The flux and rejection data for the three life tests are given in Table 4 and are plotted as a function of exposure time in Figure 5. Except for the periods shown in Figure 5, the test system was operated 24 hours per day so that exposure time and operating time are not greatly different in this plot. Over the first 150 hours using the synthetic feed solution without brightener, no decrease in rejection was observed. Over the next 150 hour period brightener was added to the feed solution at several points as shown in Table 4. A gradual but definite decrease in rejection was observed. Over the 150 hour period the rejection decreased from 96.5% to 92%. Tests with the actual plating bath solution at 17% of bath concentration showed an initial decrease in rejection, but at longer exposure times the rejection appeared to decrease much more slowly. (This behavior would be expected for a total recycle system as explained above.)

No substantial difference can be observed in the rate of flux decline for the three life tests. The discontinuity in the flux curve can be attributed to a higher feed concentration for the actual bath.

The rejection results of Figure 4 tend to confirm the suspicion that the brightener is the constituent responsible for the rejection decline. A definite decrease in rejection was observed when the brightener was added to the feed solution, but it remains to be answered as to whether the magnitude of the decrease is comparable to the decrease observed in field tests. If the brightener reacts rapidly with the membrane then the degree of degradation is a direct function of the amount of brightener fed to a given module. A total of 0.134 gal (5,380 ppm in 25 gallons) was added to the feed solution during the laboratory tests. For the recommended bath concentration of 2000 ppm vol and a drag-out of 40 gpd, the RO demonstration plant would be fed 0.134 gal of brightener in approximately 40 hours. The decrease in rejection for the laboratory tests (96.5% to 92%) is at least reasonably consistent with the decrease observed in field tests (Figure 4) for an equivalent brightener exposure.

TABLE 4. RESULTS OF LABORATORY TESTS WITH CYANIDE BATH CHEMICALS WITH AND WITHOUT BRIGHTENER, AND WITH ACTUAL BATH SOLUTION

Activity, oz/gal	Time, hr	Efficiency, percent	Plus [1] (gain)	Corrected plus [1] (gain)	% Cop. solution	Feed	Conductivity, umho/cm Deposit	Throwing power, percent
Life test with bath chemicals without brightener in the feed (8X4 Bath Concentration)								
1	12	101	1.59	1.59	58	18,000	170	93.73
	20	101	1.61	1.61	58	18,000	170	93.73
System down all stopped cooling for about 48 hrs during weekend								
1	12.5	102	1.58	1.58	58	18,000	610	95.50
1	13	102	1.59	1.59	58	18,000	610	95.50
1	13.5	102	1.60	1.60	57	18,000	630	96.50
1	14	103	1.61	1.61	57	18,000	630	96.50
1.04	15	103	1.61	1.61	58	18,000	640	96.50
Life test with brightener added to the proper feed solution (1/2 oz of Sulfonic Brightener added to 50 gal feed solution								
1.04	12	102	1.63	1.60	58.5	18,000	670	93.01
1.04	13	102	1.63	1.60	58.5	18,000	670	93.74
1.04	14	103	1.63	1.60	58.5	18,000	650	93.46
Added 1000 cc of Sulfonic Brightener								
1.06	20	104	1.67	1.90	57	19,100	640	95.76
Added 1000 cc of Sulfonic Brightener								
1.07	20	105	1.62	1.87	58	19,600	950	93.97
Added 1000 cc of Sulfonic Brightener								
1.07	10	103	1.72	1.79	58	19,100	950	93.70
1.07	12	103	1.67	1.67	58	19,100	1,070	93.73
1.07	14	103	1.66	1.66	58	19,000	1,100	93.73
Life test with Actual Bath Solution (1X4 Bath Concentration)								
1.04	Stacked tail							
1.04	10	101	1.58	1.57	57	23,000	1,150	93.75
1.04	12	101	1.60	1.57	57	23,000	1,150	93.75
Added 5 gal of water to the feed solution								
1.03	12	101	1.61	1.61	58.5	23,000	1,100	93.93
1.03	13	101	1.62	1.61	58	23,000	1,070	93.93
1.03	13	101	1.62	1.61	58	23,000	1,070	93.9
1.04	13.5	102	1.6	1.6	58	23,000	1,000	93.9
System was stopped cooling for about 11 hrs during weekend								
1.03	12	100	1.6	1.6	57	23,000	1,000	88.5
1.03	13	100	1.6	1.6	58	23,000	1,000	93.2
1.03	14	100	1.6	1.6	58	23,000	1,000	93.2
1.03	14.5	100	1.6	1.6	58	23,000	1,000	93.2
1.03	15	100	1.6	1.6	57.5	23,000	1,000	93.2
End of Tests								

1 Plus corrected to ASS gal and ETT using duPont correction factors from Technical Information Manual

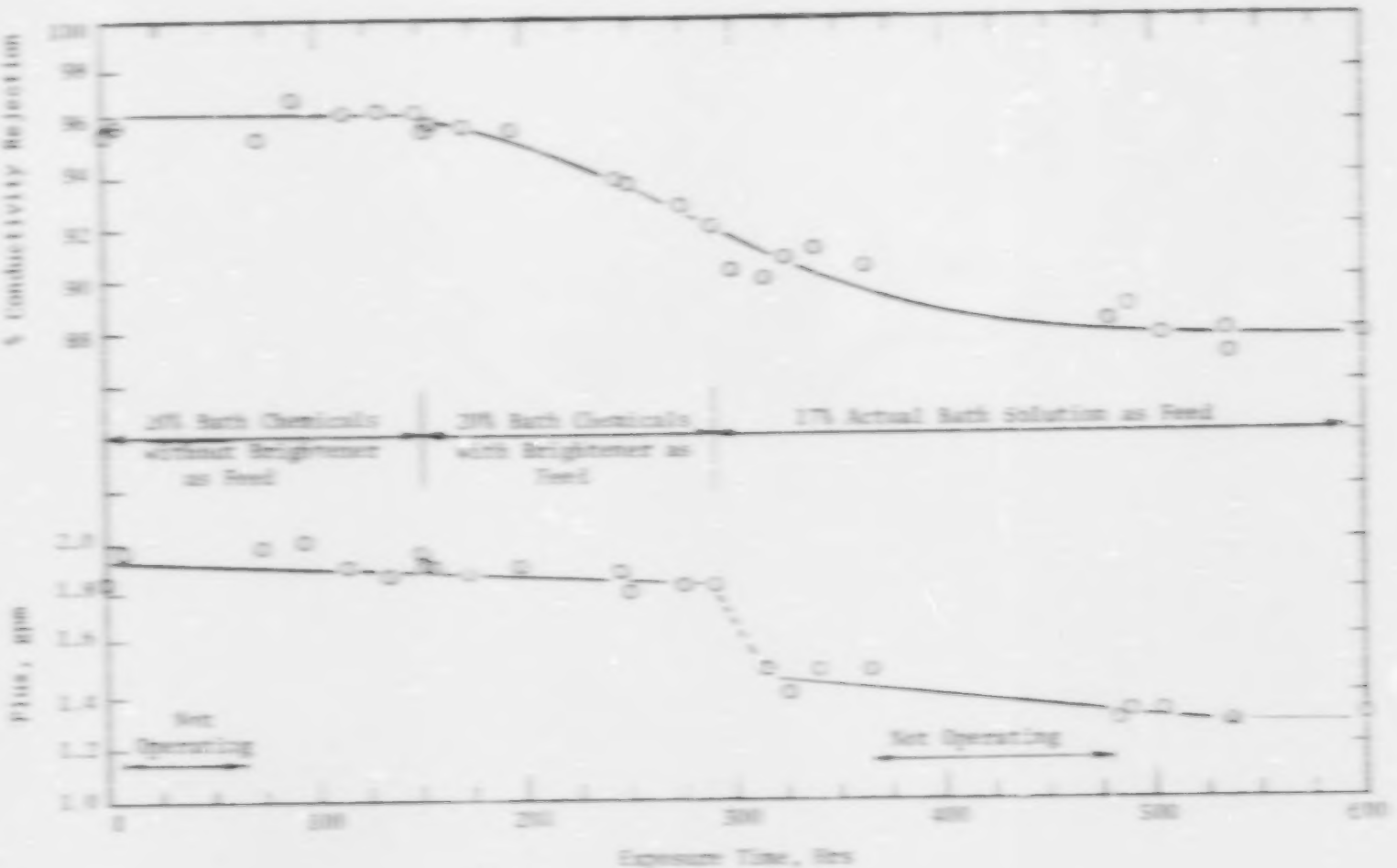

% Conductivity Rejection
Flux, gfd
20% Bath Chemicals without Brightener as Feed
20% Bath Chemicals with Brightener as Feed
17% Actual Bath solution as Feed
Not Operating
Not Operating
Operation Time, Hrs

Figure 5. Membrane Life Tests Without Brightener, With Brightener, and With Actual Plating Bath Solution.

LIFE TESTS ON MINI-PERMEATORS

Tests conducted on the full-size module were somewhat inconclusive because of the rather small drop in rejection and the small total exposure to the brightener. In order to investigate the stability of the polyamide membrane in more detail, tests were conducted with mini-permeators obtained from the Permasep Products Division of duPont.

The details of a mini-permeator are shown in figure 6. The active portion of the permeator consists of one strand (150 filaments) of polyamide hollow fibers. The strand is looped as shown, and both open ends are seated in an epoxy pot. Permeate is withdrawn at one end of the fiber strand after slicing the permeate tube to expose the open fiber ends. The normal four-inch permeator contains about 900,000 filaments so that, in terms of surface area, the mini-permeator is less than 2×10^{-4} times the size of a full-scale module.

The mini-permeators were operated at 400 psi, approximately 77^{0}F, and essentially zero percent conversion. The initial flux was on the order of 2 cc/min or less while the feed and concentrate flow rates were on the order of 1000 cc/min.

The feed solution was prepared from laboratory grade chemicals and distilled water. The bath composition, shown below, was diluted

Component	Concentration
CuCN	8.6 oz/gal
NaCN	11.9 oz/gal
NaOH	2.5 oz/gal
Rochelle Salts	4.0 oz/gal

to 20% of its original concentration and the pH was adjusted to 11.0 (maximum for the polyamide membrane) with hydrochloric acid.

The brighteners were added in considerable excess over the recommended bath concentration. A total of one pint of brightener solution was added to five gallons of feed solution giving a concentration of 25,000 ppm. This is

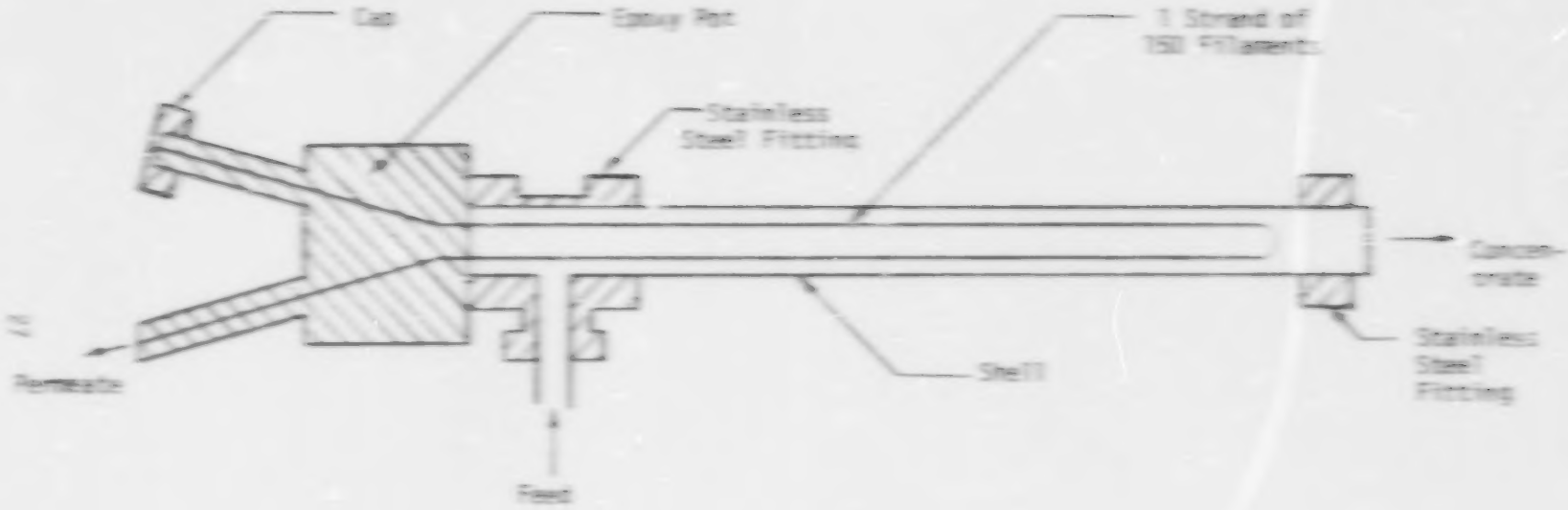


Figure 6. Schematic Diagram of Mini-permeator.

about an order of magnitude above the recommended bath concentration and about two orders of magnitude above the maximum concentration that the RO system sees.

The exposure of a mini-permeator to one pint (.125 gallons) of brightener is equivalent to the exposure of a full size permeator to 625 gallons ($.125/2 \times 10^{-4}$) of brightener. At 60 gallons per day dragout of 2000 ppm brightener, this is equivalent to an operating time at Whyco of 7,800 days or 21.5 years!

Results will be presented for three mini-permeators, each operated on a different feed solution. All feed solutions contained plating chemicals at 20% of bath concentration adjusted to pH 11.0. The first feed solution tested contained no brightener, the second contained an organic-based brightener (Allied-Kelite Isobrite 625), and the third contained a selenium-based brightener (MacDermid CI Bright Copper). (The use of these particular brighteners is not intended as an endorsement.)

Rejection data for the three feed solutions are shown in Figures 7, 8, and 9. The curves from these three figures are compared in Figure 10. The best overall performance was obtained with the feed solution containing the selenium-based brightener, and the poorest performance was obtained with no brightener in the feed. The difference in performance between the feed solutions containing the organic-based and the selenium-based brighteners is not significant.

The rejection results of Figure 10 indicate that the polyamide membrane is quite resistant to both organic-based and selenium-based brighteners. Both the concentration and exposure of the membrane to the brightener were far in excess of the concentration and total exposure a typical membrane would receive in an actual system. This conclusion would appear to contradict the results of Figure 5 which indicate a definite decrease in rejection performance of the module when the brightener is added. The difference in results may be due to deterioration of some portion of the module (in particular, the Reemay spacer) other than the polyamide fiber. (Note that the mini-permeator does not contain a Reemay spacer.) This will be discussed in more detail below.

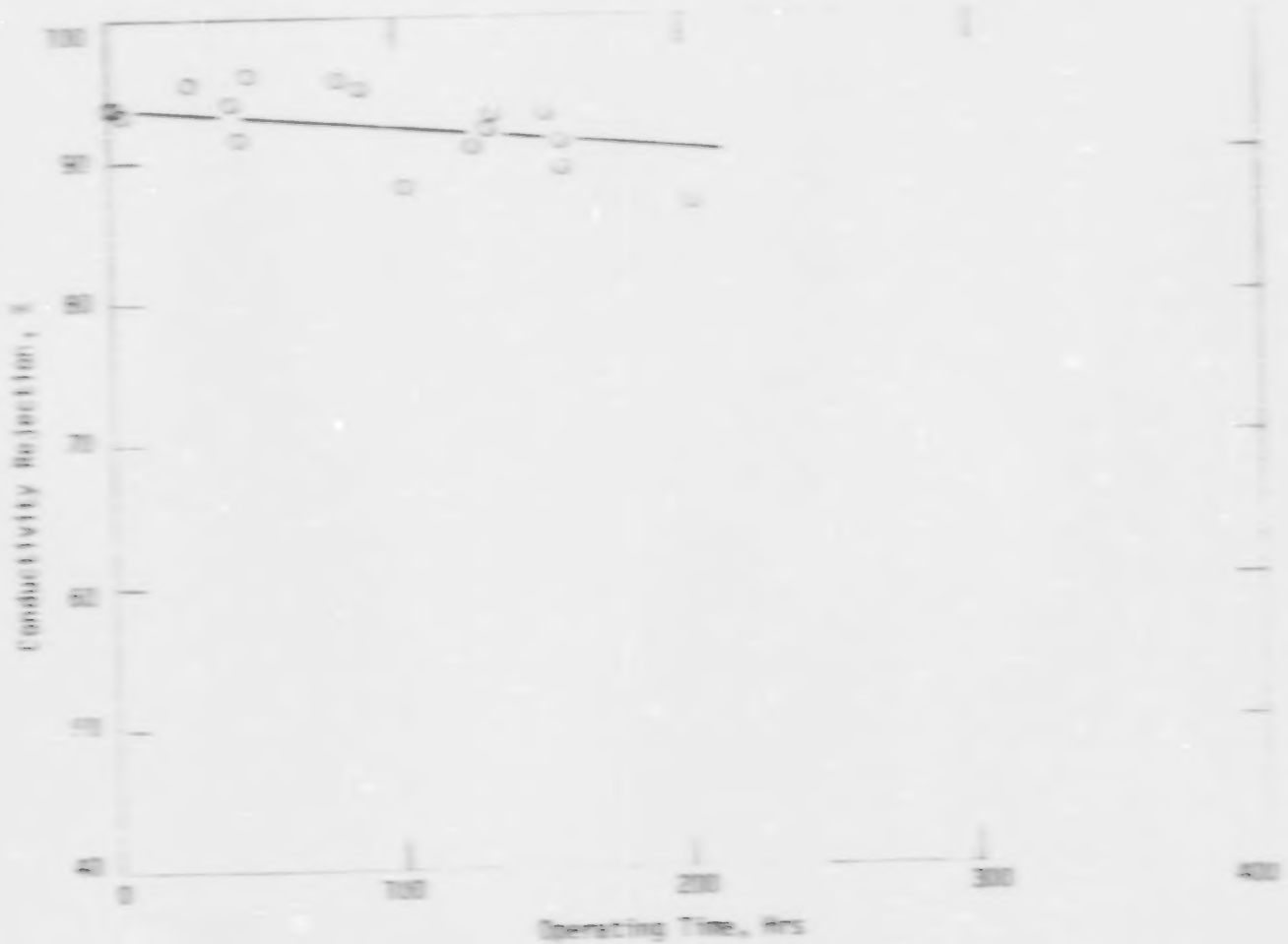


Figure 7. Mixed-permeator Conductivity Rejection vs. Operating Time Without Brightener.

100
90
80
70
60
50
40
0
100
200
300
400
Operating Time, hrs

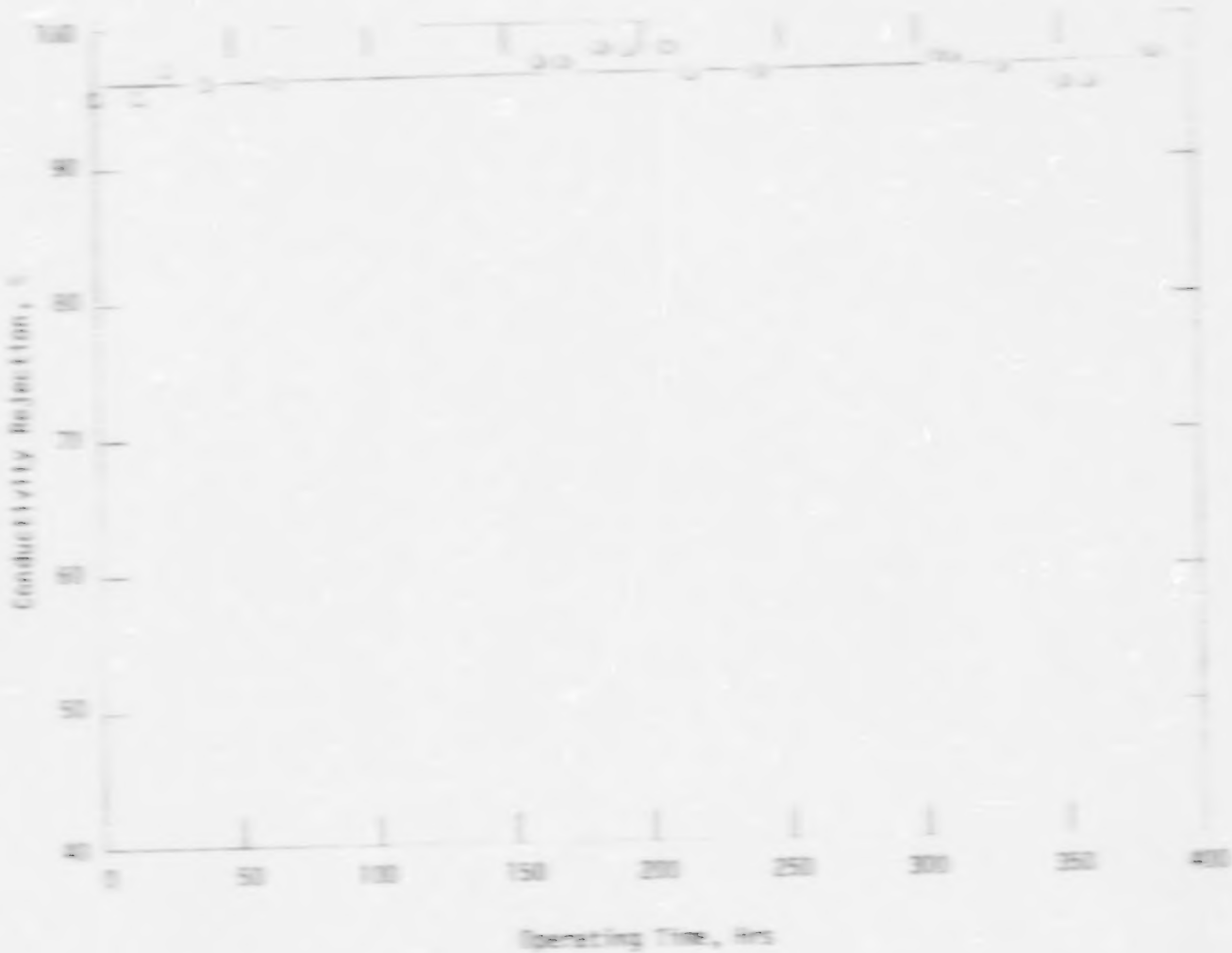


Figure 1. Mini-perfector Conductivity Rejection vs. Operating Time with Selenium-based Brightener.

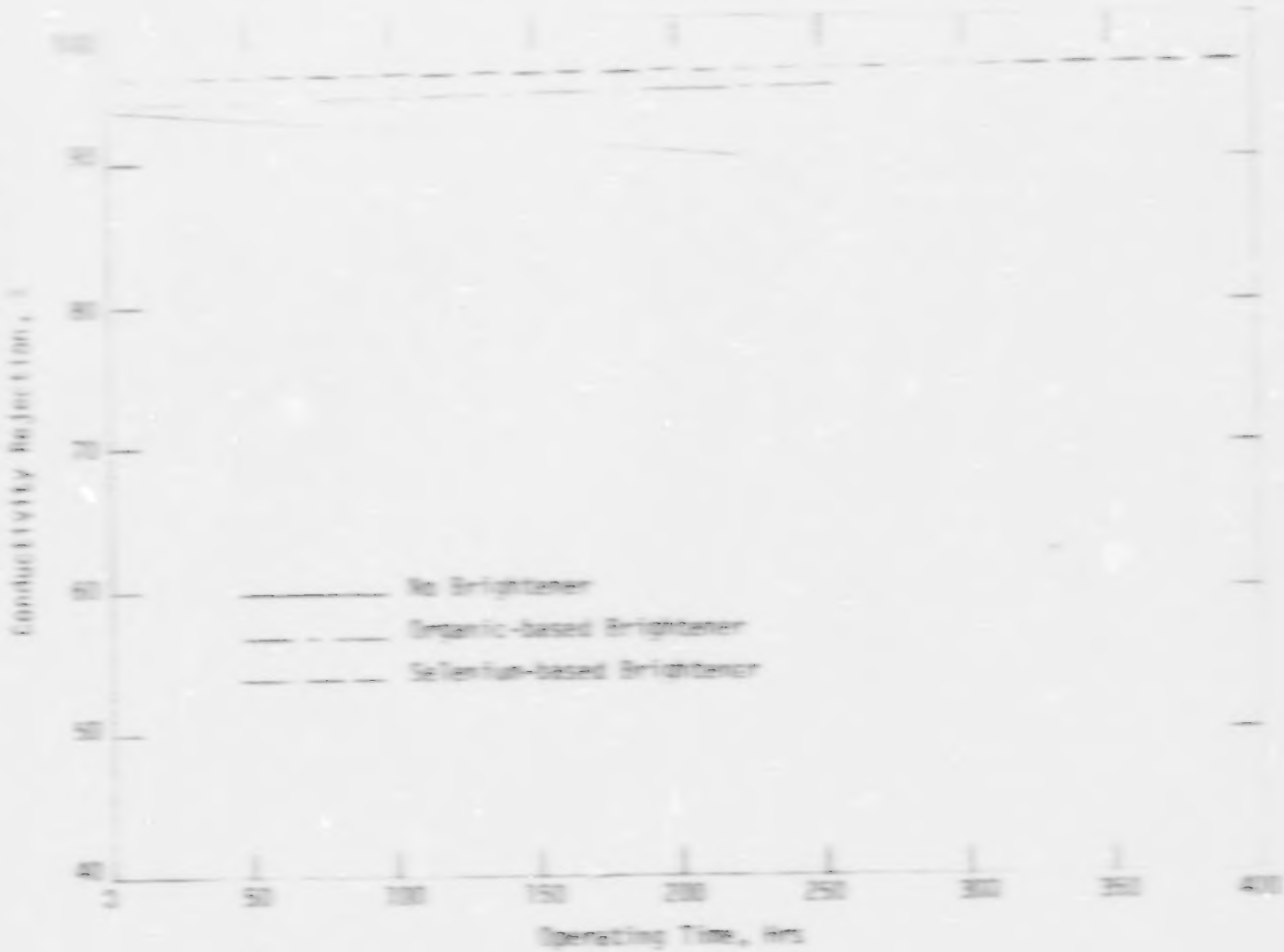


Figure 10. Comparison of Mini-perMeator Reductions for Various Feed Solutions.

LIFE TESTS ON HALF-SIZE PERMEATOR

Because of the apparent contradiction in results between the full-size permeator tests and the mini-permeator tests, further life studies were initiated using half-size B-9 permeators. The configuration of the half-size module is identical to the full-size module except that the half-size module is only about half as long. Laboratory tests were conducted with two separate modules: one operated on feed solutions containing no brighteners, the other on feed solutions containing a selenium-based brightener (Mac Dermid CI Bright Copper). The same laboratory life test system described previously was used.

Feed Solution Without Brightener

A half-size B-9 module was operated for 1360 hours on a feed solution containing plating chemicals at 20% of bath strength (pH 11) but without the brightener. The data are given in Table 5. No corrections for feed concentration, conversion, pressure, or temperature were applied to the data. The conductivity rejections are plotted as a function of exposure time in Figure 11. For these tests the operating time was very nearly the same as the exposure time since the system operated continuously. The rejection declined gradually from about 96.5% initially to an extrapolated value of 92.5% over three months (2200 hours) of exposure time.

Flux data are shown in Figure 12. The productivity dropped to about 1/2 of its initial value over the first 450 hours of exposure. The module was cleaned at that point using the procedure noted in Table 5, and the flux gradually recovered and remained close to its initial value for the remainder of the test. It is possible that the cleaning procedure removed some iron hydroxide deposits from the membrane that could have resulted from corrosion within the test system.

The data of Figures 11 and 12 indicate that the flux and rejection are quite stable to the major constituents of the bath.

TABLE 5. LIFE-TEST DATA FOR FEED SOLUTION WITHOUT BRIGHTENER

Cumulative Exposure Time (hrs)	Feed Pressure (psi)	Flux (l/m²/d)	Conversion (%)	Conductivity (as ppm NaCl) Feed ×10	Permeate ×10	Rejection (%)
76	280	1.83	45	1.2	0.9	97
77	280	1.85	45	1.3	1.5	95
91	310	2.28	56	1.2	1.2	97
99	320	1.64	40	1.3	1.6	97
115	300	1.64	40	1.3	1.2	95
123	290	1.68	41	1.0	1.0	96
140	300	1.64	40	1.4	1.0	96
147	290	1.76	43	1.2	1.5	94
211	300	1.96	48	1.2	0.9	97
219	250	1.44	35	1.4	1.2	96
235	310	1.66	41	1.3	1.0	96
260	310	1.63	39	1.2	1.2	96
283	310	1.80	44	1.6	1.3	96
331	280	1.36	33	1.3	1.6	95
339	290	1.40	34	1.3	1.3	95
356	290	1.40	34	1.3	1.4	95
385	290	1.36	33	1.2	1.6	95
432	290	1.10	27	1.3	1.0	97
452	260	.96	23	1.3	0.9	97
465	System Cleaned*					
483	300	1.32	32	1.4	0.8	96
498	270	1.28	31	2.1	0.7	97
562	300	1.68	41	1.4	0.7	95
625	340	2.32	56	1.4	0.5	98
634	310	2.00	49	1.4	0.6	98
650	310	1.92	47	1.3	0.8	97
656	340	2.00	49	1.4	0.5	97
675	330	1.76	43	1.4	0.7	95
697	340	1.68	41	1.4	0.7	96
706	340			1.4	0.6	96
721	340	1.75	43	1.4	0.6	97
730	330	1.64	40	1.4	0.7	96
804	300	1.60	41	1.4	0.9	97
913	300	1.72	42	1.6	0.9	94
949	300	1.70	41	1.6	0.9	94
954	300	1.72	42	1.4	0.7	95
988	300	1.72	42	1.4	0.7	96
1017	300	1.82	45	1.4	0.7	97
1021	300	1.80	44	1.4	0.8	96
1084	300	1.73	43	1.4	0.8	97
1092	300	1.80	44	1.4	0.9	94
1108	290	1.76	43	2.1	1.2	94
1164	300	1.84	45	2.1	1.2	94
1251	300	1.36	48	1.9	1.3	94
1284	300	1.80	46	1.9	1.3	93
1310	300	1.84	45	1.9	1.3	93
1336	290	1.76	43	2.1	1.3	94
1360	223	2.40	60	1.9	1.1	97
1422	200	2.10	61	1.9	1.5	97

* Module was flushed with a 2% solution of citric acid adjusted to pH 4.0 with ammonium hydroxide.

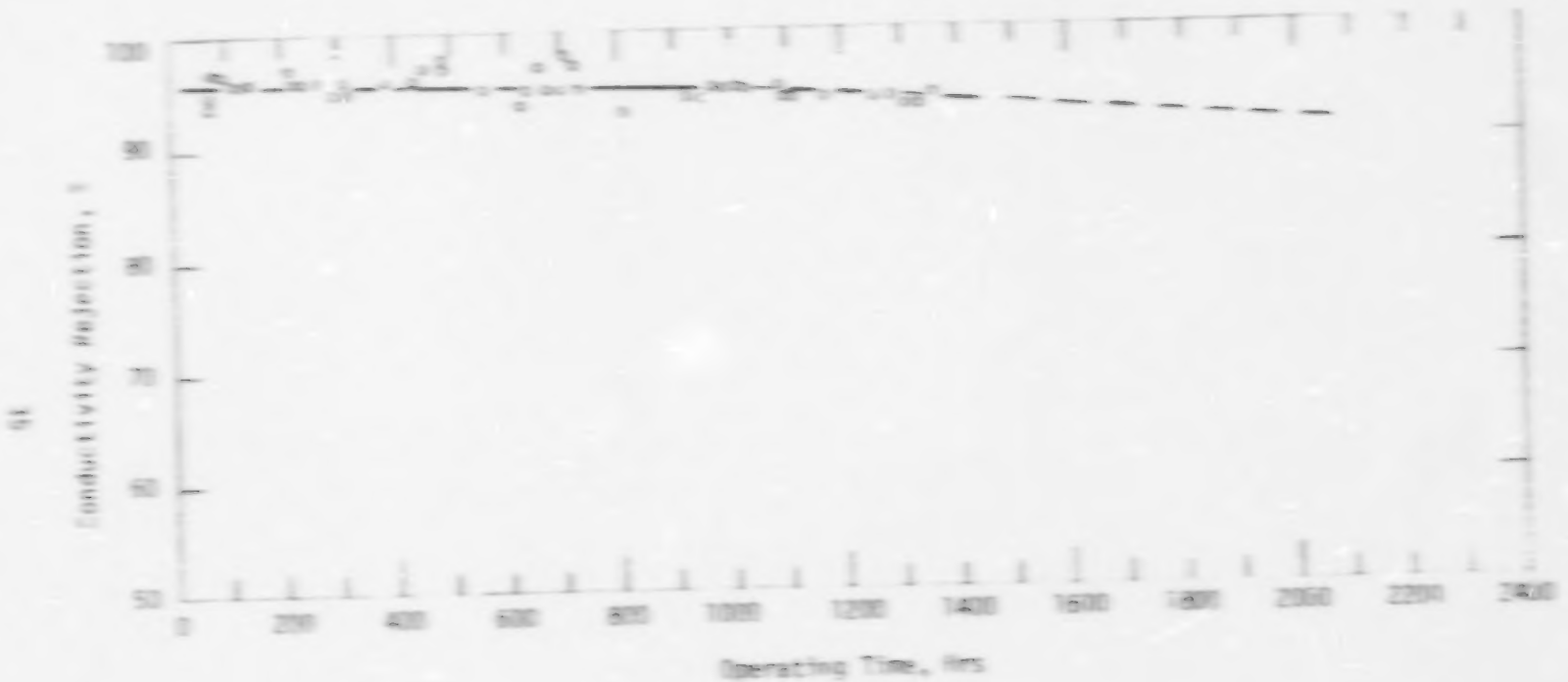


Figure 11. Conductivity Rejection vs. Operating Time for Life Test Without Brightener.

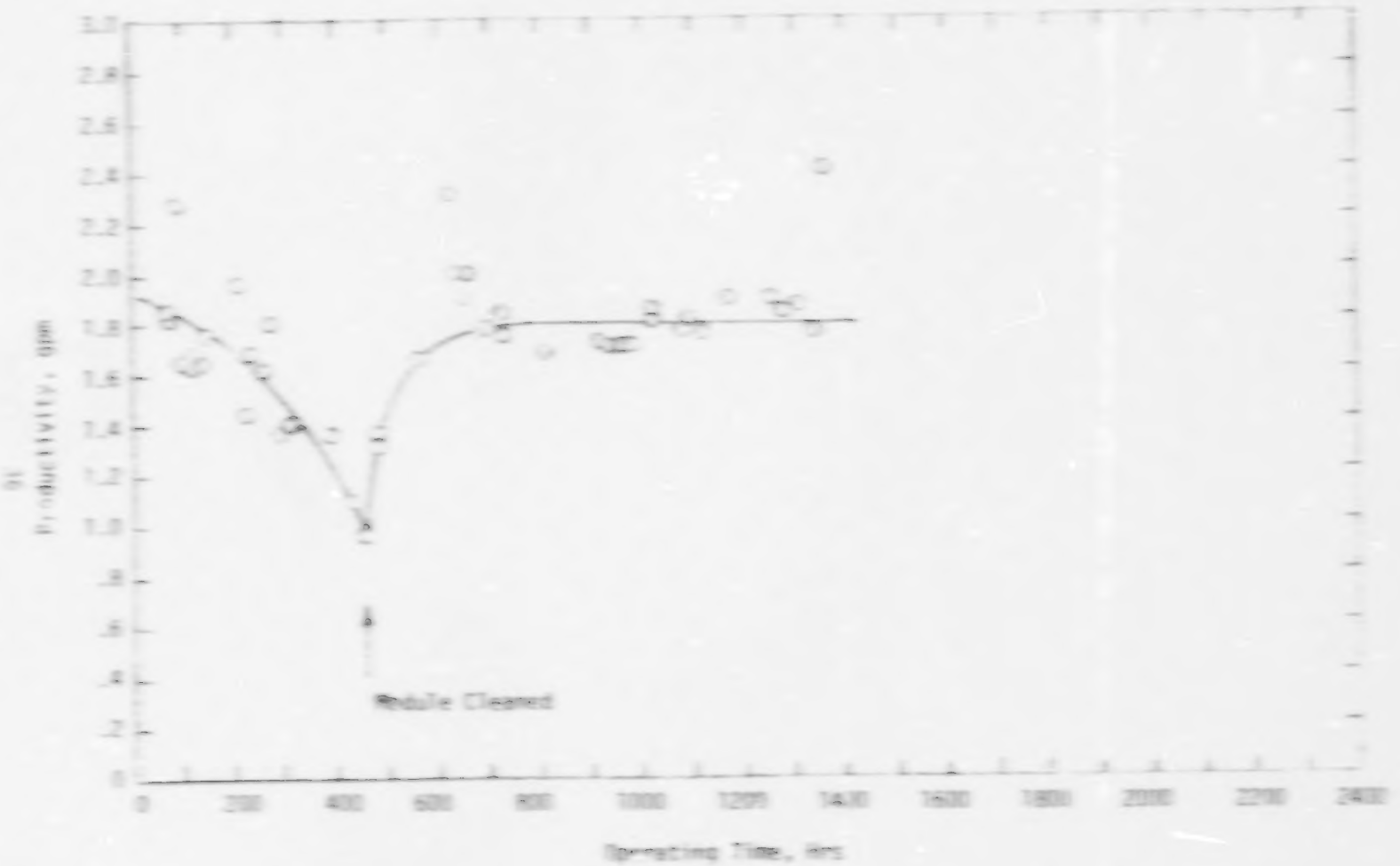


Figure 12. Productivity vs. Operating Time for Life Test without Brightener.

Feed Solution With Brightener

A half-size 8-9 module was operated on an identical feed solution to which brightener was added at various points. The data are summarized in Table 6. The uncorrected conductivity rejections are plotted as a function of exposure time in Figure 13. The notes indicate when and to what extent brightener was added.

Over the first 1222 hours enough brightener was added to the feed tank to give a concentration, after the final addition, of 17,500 ppm. This is 8.75 times the recommended concentration (2000 ppm) for the bath, and about 87.5 times the maximum concentration the RO system should see (assuming the concentrate stream is about 10% of bath strength). Therefore, in terms of brightener concentration, the life tests were severe. The total exposure after point D is 1.0 l of brightener (17,500 ppm in 56l). This is an exposure equivalent to 10 days operating time at Whyco (40 gpd dragout of 2000 ppm brightener for eight hours per day). A significant decline in rejection was observed in the field tests over 10 days (240 hours) of operating time. The results of Figure 13 indicate that the decline in rejection observed at Whyco cannot be directly attributed to the action of the brightener. The results are summarized below for equivalent exposures.

	Total Exposure	Max. Conc.	Conductivity Rejection Decline
Whyco (over first 240 hours)	1 l	200 ppm	90% to 65%
Laboratory Simulation	1 l	17,500 ppm	97% to 92%

In order to determine whether the brightener had any detrimental effect at all on module performance, the module was exposed to a massive dose of brightener (1.5 gal brightener in 10 gal water) at point E of Figure 13. At point F the brightener solution was replaced by a solution containing plating chemicals at 20% of bath strength (without brightener), and the rejection compares favorably with the rejection at point D, before the massive brightener dose.

TABLE 6. LIFE-TEST DATA FOR FEED SOLUTION CONTAINING BRIGHTENER

	Cumulative Exposure Time (hrs)	Feed Pressure (psi)	Flux (l/min)	Conversion (%)	Conductivity (as ppm NaCl) Feed x10	Conductivity (as ppm NaCl) Permeate x10^{-3}	Rejection (%)
*	0	RE-					
	20	300	1.12	28	3.4	2.2	94
	44	300	1.20	30	3.4	2.0	94
	68	300	1.17	28	3.4	2.0	94
	92	300	1.12	28	3.1	1.8	95
	117	300	1.16	29	3.5	2.0	92
	140	305	1.04	26	3.6	1.4	94
	165	310	1.28	32	3.4	1.4	94
	189	310	1.20	30	3.4	1.4	94
	213	275	.80	20	3.4	1.0	94
	236	285	0.80	22	3.4	1.2	94
	261	290	0.96	24	3.4	1.6	93
	285	290	...	...	3.4	1.5	93
	309	290	0.96	24	3.4	1.5	93
A *	333	290	0.96	24	3.4	1.7	93
	357	300	1.16	29	3.3	2.0	91
	404	300	0.88	22	3.3	1.9	92
	428	300	0.90	22	3.3	1.9	92
	453	300	0.90	22	3.3	1.9	92
B *	549	300	0.96	24	3.3	1.6	93
	573	300	0.90	22	3.3	1.6	93
	597	300	0.92	23	3.3	1.6	93
	621	300	0.80	20	3.3	1.5	93
	645	300	0.80	20	3.3	1.5	93
	669	300	0.84	21	3.4	1.5	93
	693	300	0.84	21	3.4	1.5	93
	717	300	0.80	20	3.6	1.5	93
C *	749	300	0.80	20	3.5	1.4	93
	840	300	0.80	20	3.6	1.3	93
	869	300	0.80	20	3.5	1.4	93
	894	300	0.80	20	3.5	1.4	93
	909	300	0.72	18	3.5	1.4	93
	933	300	0.72	18	3.5	1.4	93
	1037	310	0.64	16	3.5	1.4	93
	1060	310	0.64	16	3.6	1.4	93
	1079	310	0.66	17	3.6	1.5	93
	1107	310	0.68	17	3.7	1.5	93
D *	1177	320	0.56	14	3.7	1.7	93
	1205	320	0.59	15	3.7	1.6	93
E *	1272	310	0.67	17	3.6	1.6	93
	1223	323	3.5	88	0.12	0.31	74
	1224	320	3.5	88	0.11	0.32	71
	1241	325	3.6	90	0.11	0.35	69
	1263	320	3.8	95	0.07	0.32	54
	1264	330	3.6	89	0.047	0.13	69
	1265	330	3.6	90	0.038	0.13	64
	1329	330	3.4	85	0.038	0.09	76
	1330	330	3.5	88	0.060	0.12	85
	1379	330	3.48	87	0.060	0.27	55

TABLE 6 (continued)

Cumulative Exposure Time (hrs)	Feed Pressure (psi)	Flux (l/min)	Conversion (%)	Conductivity (as ppm NaCl) Feed x 10^{-4}	Conductivity (as ppm NaCl) Permeate x 10^{-3}	Rejection (%)
1507	320	1.20	80	0.039	0.09	77
1509	360	1.6	80	0.036	0.11	69
1529	350	1.52	88	0.036	0.09	75
1554	350	1.60	90	0.036	0.1	69
1575	350	1.24	81	0.036	0.09	75
1652	350	1.36	84	0.036	0.11	69
F = 1652	350	0.96	24	2.6	2.1	92
1673	320	0.96	24	2.4	2.0	88
1676	320	0.89	20	2.4	2.7	89
1693	350	1.56	39	1.6	1.3	92
1700	340	1.52	38	1.6	1.4	91
1708	350	1.52	38	1.5	1.5	89
G = 1708	350	1.12	28	2.4	2.7	89
1814	350	1.12	28	2.4	3.0	88
1830	350	1.12	28	2.4	3.1	87
1952	350	1.12	28	2.7	3.6	87
1981	350	1.12	28	2.4	3.6	86
1999	350	1.12	28	2.4	3.6	85
H = 2071	350	1.12	28	2.4	3.7	84
2096	350	1.32	33	1.8	2.7	86
2150	350	1.30	32	1.7	2.0	88
2760	350	1.40	35	1.7	2.8	83
2408	350	1.24	31	1.7	2.7	84

* Initial Brightener Concentration: 145 ml in 58l solution = 2,500 ppm

A 290 ml Brightener Added (7,500 ppm total)

B 290 ml Brightener Added (12,500 ppm total)

C 145 ml Brightener Added (15,000 ppm total)

D 145 ml Brightener Added (17,500 ppm total)

E 1.5 Gal Brightener plus 10 gal Water

F 20% Plating Chemicals, No Brightener, with Plating

G 1% Brightener Added (10,000 ppm), with Plating

H 1.9% Brightener Added (30,000 ppm), with Plating

Figure 11. Conductivity Reduction vs. Exposure Time for Life Test with Antifreeze.

Electrical Antifreeze Characteristics: 50% wt/wt in DDI solution = 2,500 ppm

Antifreeze	Initial Conductivity (μmho/cm)	Conductivity after 30 days (μmho/cm)	Conductivity after 60 days (μmho/cm)	Conductivity after 90 days (μmho/cm)	Conductivity after 120 days (μmho/cm)	Conductivity after 150 days (μmho/cm)	Conductivity after 180 days (μmho/cm)
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Prestone Anti-Freeze/Coolant	1.15	1.15	1.15	1.15	1.15	1.15	1.15

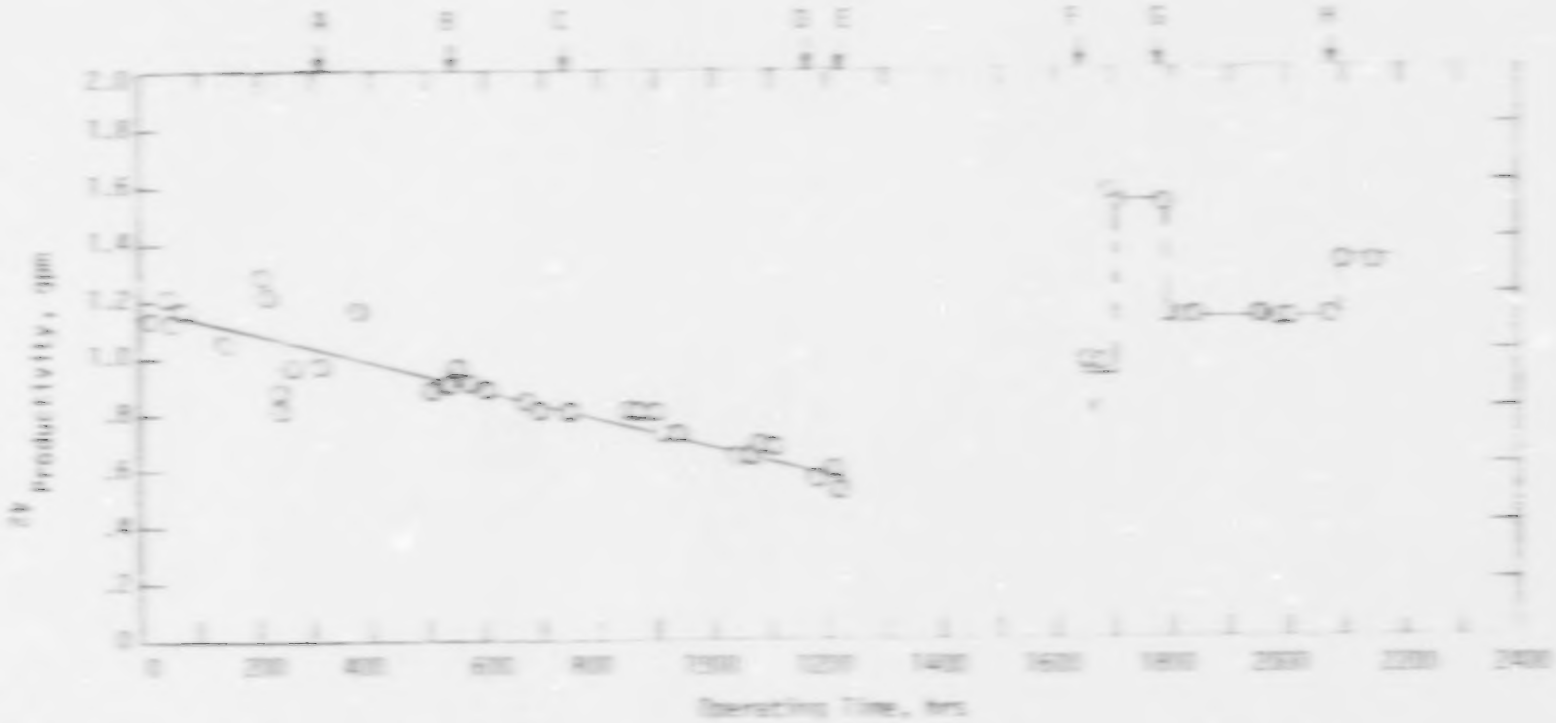
Exposure Time, hrs

It was hypothesized that the difference in results between the Whyco field test and the laboratory test was associated with the presence of an electric field in the Whyco plating tank. This field could affect the valence state of selenium thus making it more reactive toward the membrane. To simulate the plating process in the laboratory tests, a copper-plate anode and a stainless-steel-pipe cathode were mounted in the feed tank. A DC power supply operated at 1.5 volts and 1/2 amp was used to plate copper onto the cathode. The decline in conductivity rejection with plating is shown in Figure 13 beyond point F. Between points F and G the feed solution contained no brightener. Brightener was added at points G and H. The rate of decline in rejection is about 4.7 times greater with plating than without.

The productivity of the module during the life tests with brightener is shown in Figure 14. There is a definite decline in flux over the first 1222 hours to approximately one-half of the initial value. However, after the massive dose of brightener the flux recovered and remained stable although the level varied somewhat at the points where the life test was interrupted for NaCl tests. The variation in flux level could be the result of flushing during the NaCl tests or of variations in operating conditions before and after the life test interruption.

Standard sodium chloride rejection tests were conducted (400 psi, 77°F, 75% conversion, 1500 ppm feed) to follow the membrane performance after the massive brightener dose. The NaCl rejection is shown as a fuction of operating time in Figure 15. Over the first 1222 hours the NaCl rejection declined only slightly from the factory test value of 95%. When the module was exposed to the massive brightener dose (point E) the rejection declined substantially (from 93% to 81%). This indicates that the brightener can indeed attack the module if the total exposure and/or concentration are sufficiently great.

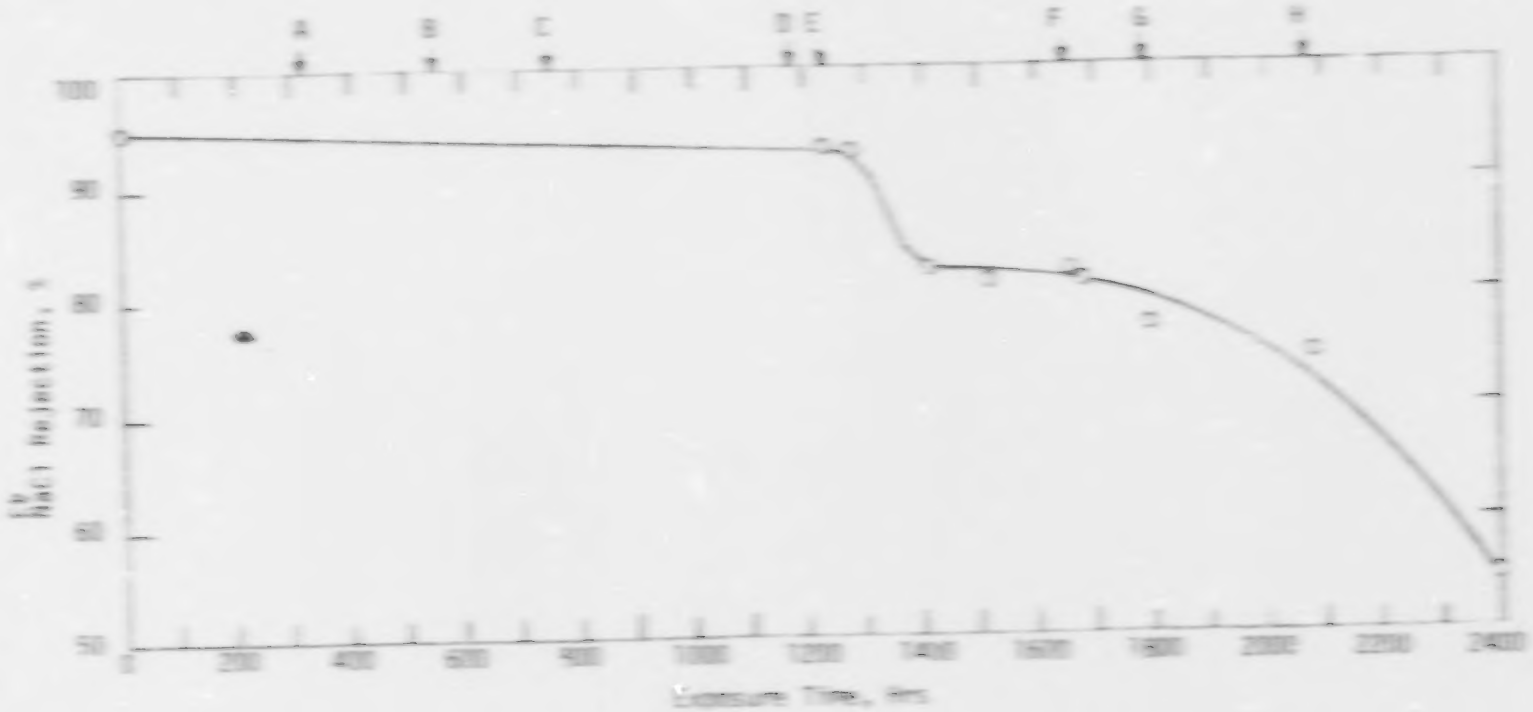
The decline in rejection when plating was on-going in the feed tank (both with and without brightener) is very interesting. This suggests that the plating process does have some effect on the membrane performance. Comparing the magnitude of the rejection decline for NaCl (Figure 15) and plating chemicals (Figure 13), the greater decline for NaCl is to be expected. When rejection declines, the species that have the lowest initial rejection (small univalent ions such as sodium and chloride) have the highest rate of decline. Large multivalent ions



[Initial Brightener Concentration: 145 ml in 5% solution = 7,500 ppm]

A 290 ml Brightener Added [7,500 ppm Total]
B 290 ml Brightener Added [12,500 ppm Total]
C 145 ml Brightener Added [15,000 ppm Total]
D 145 ml Brightener Added [17,500 ppm Total]
E 1.5 gal Brightener plus 10 gal Water as Feed
F 200 Plating Chemicals, No Brightener, with Plating
G 1 l Brightener Added [10,000 ppm], with Plating
H 1.5 l Brightener Added [21,000 ppm], with Plating

Figure 14. Productivity vs. Exposure Time for Life Test with Brightener.



[Initial] Brightener Concentration 145 ml in 5% solution = 2,500 ppm

A 290 ml Brightener Added [7,500 ppm Total]
B 290 ml Brightener Added [12,500 ppm Total]
C 145 ml Brightener Added [15,000 ppm Total]
D 145 ml Brightener Added [17,500 ppm Total]
E 1.5 gal Brightener plus 10 gal Water as Feed
F 20% Plating Chemicals, No Brightener, with Plating
G 1 l Brightener Added [10,000 ppm], with Plating
H 1.5 l Brightener Added [30,000 ppm], with Plating

Figure 15. Sodium Chloride Rejection vs. Exposure Time for Life Test With Brightener.

(plating solution) are initially rejected very well and show a slow rate of decline. The results of Figure 13 are sufficiently interesting to warrent a more detailed investigation of the interaction between brighteners (with and without plating) and the B-9 membrane. It may be that the massive brightener dose initiated the rejection decline, and the same rate of decline may have occurred without any plating in the feed tank.

The module used in the brightener tests (Figures 13 - 15) was returned to duPont for destructive analysis. Unfortunately, the fiber length in a half-size module is too short to fabricate mini-permeators. Therefore permeation tests on the fibers themselves could not be made. The findings were:

1. The NaCl rejection of the module,upon receipt by duPont, was only 35% as measured under standard conditions (400 psi, 77°F, 75% conversion, 1500 ppm feed concentration).

2. There was no evidence of any mechanical defects.

3. There was no evidence of any scaling, particulates, or foulants in the fiber bundle.

4. There was no significant deterioration in the tensile properties or collapse resistance of the fibers.

5. The Reemay spacer showed significant deterioration in physical properties and was visibly damaged to such an extent that very poor flow distribution of feed throughout the fiber bundle would occur during normal operation.

6. Dye tests performed on the polyamide fibers to check for skin damage showed a slight positive indication of skin damage. The subjective evaluation of these tests indicated that a rejection as low as perhaps 60% could be explained by the amount of skin damage observed, but there was insufficient skin damage to account for a rejection of 35%.

These results indicate that the major cause of deterioration in module performance may be attack of the Reemay spacer/flow-distributor by the brightener rather than attack of the membrane itself. This will be discussed in more detail in Section VI.

SECTION V

PHASE II: FIELD TESTS AT NEW ENGLAND PLATING

GENERAL

Because of problems encountered in the plating operation at Whyco Chromium Co., the RO field tests at that site had to be discontinued. These problems were not directly related to the presence of the RO unit. After approximately six-month's delay, a new field test site was located: New England Plating Co., Inc., Worcester, Massachusetts and tests were resumed on a small copper cyanide bath at this new location.

As shown in Table I, the copper cyanide bath at New England Plating is similar in composition to the Whyco bath. The major differences are that New England Plating uses a potassium bath rather than sodium, and the pH is higher. The same selenium-based brightener (MacDermid CI Bright Copper) is used at both locations.

The plating line was a manual rack line which operated one shift per day. The plating tank was about 450 gallons in size. It was preceeded by a two-stage rinse (after an acid dip) and was followed by a two-stage rinse, an acid dip, and a final rinse. Only one type of work was plated in this operation: smooth round discs. Since the dragout for these parts was uncharacteristically low, a drip-tank of plating solution was installed over the rinse during the final week of operation to simulate a higher continuous dragout from the bath.

Because of the great difference in size of the two plating lines, the demonstration unit used at Whyco was greatly oversized for New England Plating. Therefore a smaller system was designed and installed at New England Plating. This system was operated over a four month period during which membrane performance was monitored. During the last two months of operation the system ran largely unattended. Sodium chloride tests were performed once every two weeks during this period to monitor membrane performance.

EXPERIMENTAL

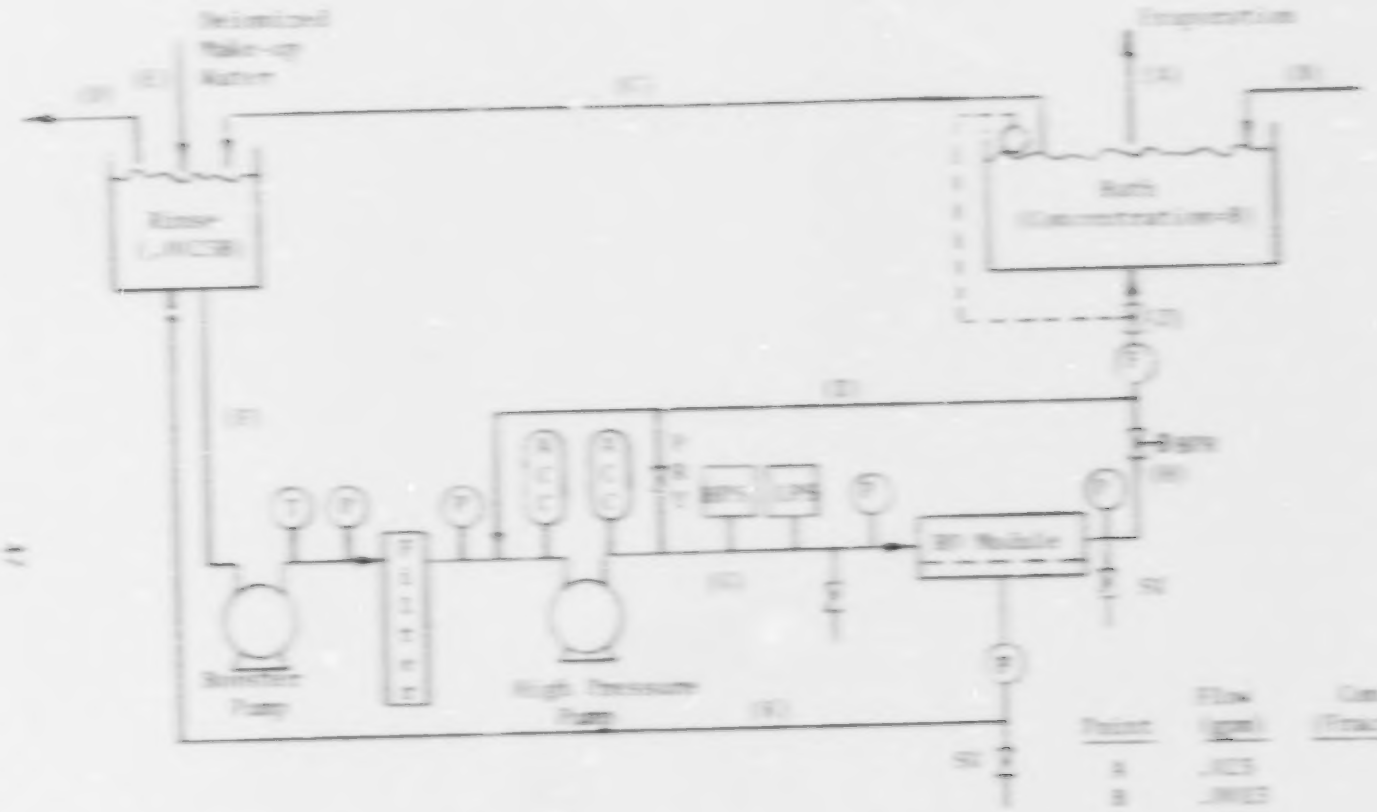
Field Test System

A simplified flow schematic of the plating line and RO field demonstration unit is shown in Figure 16. Feed was pumped from the rinse tank by a booster pump (Flotec CGP6 centrifugal) and passed through a one-micron cartridge filter. The pressure of the filtered feed was increased to the desired operating pressure by a high-pressure, positive-displacement pump (Yarway Cyclophram Model 072). Pressure pulsations were dampened by accumulators on the pump suction and discharge. The feed was separated into a concentrate stream and a permeate stream by a half-size duPont B-9 Permasep® permeator (model B420-021). The permeate stream from the RO module was returned directly to the rinse tank. The concentrate stream passed through a back-pressure regulator (BPR) which controlled the operating pressure in the module. Most of the concentrate stream was recycled to the suction of the high-pressure pump to maintain a sufficiently high flow through the module. A float valve operating off the bath level returned concentrate to the bath as needed to compensate for evaporation.

Pressures were measured before and after the filter to determine when the cartridge should be replaced. Pressures were also measured before and after the RO module to determine the operating pressure and the pressure drop. The system was protected against overpressurization by a pressure relief valve and high pressure switch, and the pump was protected against running dry by a low pressure switch.

The flow rates of the permeate and concentrate-to-bath were measured. In addition the output of the high pressure pump was measured on several occasions by the "bucket-and-stopwatch" technique and was found to be constant at 1.03 (± .02) gpm. The concentrate recycle flow was determined by difference.

Samples of the feed, permeate, and concentrate were obtained through the sample valves shown in Figure 16. Because of the variations in the rinse concentration, samples were generally taken during the afternoon after the concentration in the rinse tank had reached a steady value for the day.



Point	Flow (gpm)	Concentration (Fraction of Bath)
A	.023	0
B	.0023	0
C	.0023	0
D	.0423	.00239
E	.023	0
F	.465	.00239
G	1.0	.004548
H	.14	.0348
I	.117	.0348
J	.023	.0343
K	.44	.0039419

Figure 16. Flow Schematic for New England Plating Field Test System.

Permeate samples were taken first since the loss of permeate would not affect the concentration of either the feed or concentrate. Feed samples were taken second since the feed concentration is used in calculating rejection. Concentrate samples were withdrawn third and could have been low in concentration if a large feed sample was withdrawn just previously. The conductivity in the rinse tank was continuously monitored by a conductivity probe and recorder.

Calculated flows and concentrations are shown at various points in Figure 16. The evaporation from the bath was estimated by measuring the drop in bath level with time when no make-up water was added. The drag-out rate was estimated by measuring the increase in copper concentration with time in a still rinse following the bath. The calculated flows (gallons per minute) and concentrations (fraction of bath concentration, B) are based on an assumed rejection of 90%, a conversion of 75%, and a maximum high-pressure pump output of 1.0 gpm. The calculated rinse concentration is 0.05 of the bath concentration which meets the requirement of a two-order-of-magnitude drop in concentration for each rinse. This requirement was agreed to by New England Plating (and also by Whyco in the first field test). The permeate from the RO module was returned to the first rinse since its concentration was too high to be returned to a second or third-stage rinse. The rinse shown in Figure 16 was inserted into the line for the purposes of the RO demonstration. It was followed by a two-stage counter-current rinse in order to assure well-rinsed parts regardless of the performance of the RO system.

In addition to operating the unit in the normal mode shown in Figure 16, the module was periodically tested with a standard 1500 ppm NaCl solution at fixed conditions. For these tests the NaCl solution was mixed in an auxiliary tank. Feed to the RO system was withdrawn from the tank, and the permeate and concentrate were returned to the tank. (This mode of operation is identical to that for the life tests described in Section IV). When steady state was reached feed and permeate samples were analyzed for conductivity.

Operating Conditions

The duPont Technical Information Manual for Permasep® products recommends that the B-9 module be operated at 400 psi and 25 to 90% conversion. The conversion is defined as the ratio of permeate flow to feed flow. Conversion is limited to 90% in order to maintain a good flow distribution of feed through the fiber bundle. If it is assumed that this limit is based on the rated productivity of the module (1.25 gpm of permeate for the half-size module), the rate of concentrate withdrawal should be 0.14 gpm to maintain sufficient flow through the fiber bundle.

Since the pump output was only one gallon per minute the module had to be operated considerably below the 400 psi optimum in order to decrease the permeate flow rate to some reasonable fraction of the feed flow rate. Using the criterion of a 0.14 gpm minimum concentrate withdrawal rate, the pressure should be decreased to the point where the permeate flow rate is 0.86 gpm (86% conversion).

For the most part conversions ranged from 73 to 90% with an average of 84%. The pressure varied from 135 to 205 psi with an average of 180 psi. For the data reported, the feed temperature varied from 72 to 80°F.

For measurements on a standard NaCl feed solution, the average operating conditions were: conversion 78%; pressure 185 psi, and temperature 79°F.

Assays

Assays were performed for conductivity, pH, total solids (TS), copper, and free cyanide. Most of the conductivities were measured with a battery-operated hand conductivity meter, although in the field, conductivity was often measured with the probes to the conductivity recorder. Good agreement was obtained with the hand meter. All other assays were performed by the Walden Research Division of Abcor, Inc. A pH meter was used for pH, a gravimetric technique for total solids, atomic absorption for copper, and an ion selective electrode for free cyanide.

FIELD TEST RESULTS

Mechanical Operation

Aside from a few minor problems, the mechanical operation of the system was satisfactory. As usual, problems that were encountered were associated with the high-pressure pump. The original pump (which had been used for about 1000 hours previously) had to be replaced after about 250 hours of operating time. Pressure pulsations associated with the high-pressure pump were, at times, excessive but could be controlled by careful bleeding of all air from the lines and keeping the accumulators charged to the proper pressure.

The temperature build-up in the rinse and feed to the RO system (mainly because of pump energy input in a closed loop) was less than observed at Whyco. This can be accounted for by the difference in number and type of pumps and by the lower ambient temperatures at New England Plating. The maximum observed temperature of the feed to the RO system, during an operating period from mid-August to late October, was 89°F. This is comfortable below the maximum recommended operating temperature (95°F) of the B-9 module.

The level of suspended solids in the plating bath and rinse tank was very low. The cartridge filter did not require replacement, and no significant increase in pressure drop across the filter was noted during the entire field test.

Bath and Rinse Concentrations

The plating bath was analyzed for copper metal, free cyanide and caustic twice weekly by New England Plating and additions based on these analyses were made twice weekly if necessary. Bath samples were obtained periodically throughout the field test and analyzed by the Waldon analytical laboratory in order to verify that the bath composition remained constant. The results of these analyses are given in Table 7. For the most part the bath composition remained quite constant. The most notable exception is the free cyanide, and this may be the result of the analyses rather than an actual change in bath concentration.

TABLE 7. BATH CONCENTRATIONS AS A FUNCTION OF OPERATING TIME.

Cumulative Operating Time (hrs)	Total Solids (mg/l)	Copper (mg/l)	Free Cyanide (mg/l)	Conductivity (μmhos/cm)	pH
72	222,000	19,000	1,600	290,000	13.3
48	236,000	24,000	1,600	290,000	13.2
105	329,000	44,000	*****	250,000	13.1
138	348,000	46,000	*****	280,000	13.2
160	339,000	43,000	*****	270,000	13.2
225	335,000	46,000	*****	270,000	13.2
326	326,000	42,000	*****	260,000	13.2
418	331,000	42,000	*****	250,000	13.2
487	239,000	43,000	10,000	260,000	13.4
575	236,000	46,000	8,200	270,000	13.4
644	245,000	49,000	8,800	290,000	13.5
736	239,000	49,000	10,000	260,000	13.4
809	247,000	49,000	10,000	270,000	13.3
922	244,000	47,000	22,000	240,000	13.4
967	257,000	44,000	31,000	280,000	13.3
1061	255,000	46,000	19,000	285,000	13.4
1130	233,000	40,000	19,000	250,000	13.3

Rinse concentrations are given in Table 8 and depend primarily on the amount of dragout from the bath prior to sampling. Starting at 967 hours a drip tank was installed to continuously add bath to the rinse. During this period rinse concentrations were significantly higher than before the drip tank was installed.

Flux

Data Correction - Flux is defined as the rate at which permeate passes through a unit area of membrane surface when operated under specified conditions. The flux is given by the equation:

$$J_1 = K_1 (\Delta P - \Delta \Pi) \qquad (1)$$

where:

J_1 = Flux (usually reported in gallons per sq. ft. per day)
K_1 = Constant (dependent on membrane properties and temperature)
ΔP = Difference in applied pressure across the membrane
$\Delta \Pi$ = Difference in osmotic pressure across the membrane.

In general the pressure and osmotic pressure on the permeate side of the membrane are negligible relative to their respective values on the feed side. Equation (1) then simplifies to:

$$J_1 = K_1 (P - \Pi) \qquad (2)$$

where P and Π are, respectively, the applied and osmotic pressure on the feed side of the membrane. When significant conversion occurs the average feed-side osmotic pressure must be used in equation (2).

The constant, K_1 is directly proportional to the diffusivity of water through the membrane. As the temperature increases, the diffusivity increases, and, by equation (2), the flux increases. All fluxes were corrected to a temperature of 77°F using empirically determined data for the B-9 module from the Technical Information Manual.

TABLE 8. RINSE CONCENTRATIONS AS A FUNCTION OF OPERATING TIME

Cumulative Operating Time (hrs)	Total Solids (mg/l)	Copper (mg/l)	Free Cyanide (mg/l)	Conductivity (umhos/cm)	pH
22	319	50		450	10
48	203	29		270	9.8
105	236	44		470	10.1
130	102	10		240	10.0
180	182	40		380	10.5
225	201	28		500	10.4
326	140	13		260	10.4
416	60	9		120	10.0
467	310	40	29	600	10.6
575	195	27	13	270	10.1
644	291	47	29	430	10.7
736	10	3.7	2.7	42	9.6
809	465	73	39	900	10.6
922	303	49	55	600	10.1
967	895	148	88	1500	10.7
1061	1206	204	110	2000	11.0
1130	1689	288	110	3300	11.6

Flux decreases with increasing feed concentration and conversion (increasing π) as shown by equation (2). For dilute solutions as encountered in the field tests, the osmotic pressure is almost negligible compared to the applied pressure. All flux data were corrected to a feed concentration of 1500 ppm using correction factors from the Technical Information Manual. These correction factors were based on sodium chloride solutions so are not strictly applicable to plating solutions. However, the correction was only minor: in only two cases did it exceed 4%.

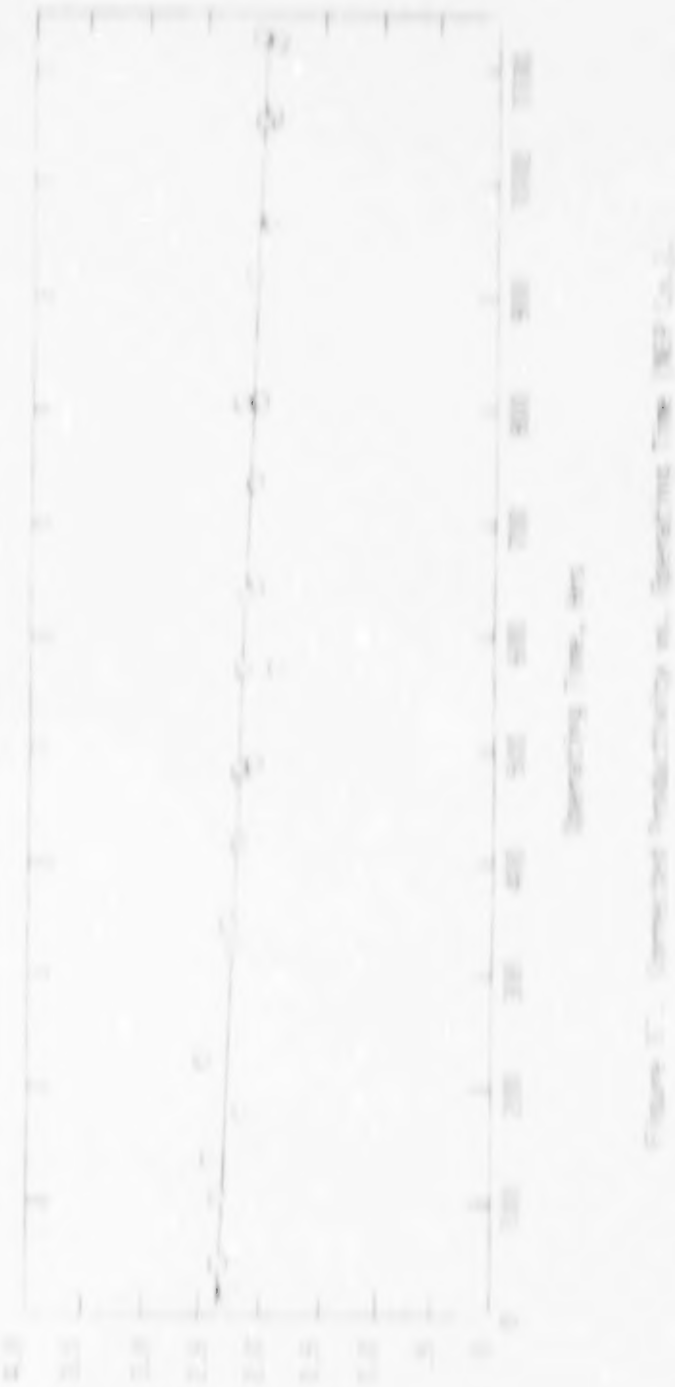
The flux is quite strongly dependent on operating pressure, and since the module was operated significantly below its maximum (optimum) pressure, a rather substantial correction factor (on the order of 100%) was applied to correct the flux to 400 psi. This correction factor was taken from the duPont Technical Information Manual and closely approximated a direct proportionality to ΔP as given by equation (2) (with π negligible).

Normal Operation - Flux data for the field demonstration are given in Table 9 and Figure 17. The flux is presented in terms of the module productivity (gpm of permeate). The operating time (pressurized operation on plating waste) during which flux and rejection were measured for plating rinse water was 1130 hours (47 days). The corresponding exposure time (pressurized and non-pressurized exposure to plating waste) was 1500 hours (62 days). The unit was operated for a total of 100 days, but data were not obtained on the flux and rejection of plating salts during the latter stages of operation. The flux (corrected to 400 psi, 75% conversion, 1500 ppm feed concentration, and 77°F) decreased only slightly, from 2.3 gpm initially to 2.0 gpm after 1130 hours.

A decrease in flux is usually attributed either to membrane compaction or fouling. The observed decrease (15% in two months) is greater than expected for compaction (5% in one year at these conditions). It is therefore possible (based on these data) that some fouling occurred. In many cases foulants can be removed by a simple cleaning procedure. However, no attempt was made to clean the module following the field test.

TABLE 9. MODULE PRODUCTIVITY AS A FUNCTION OF OPERATING TIME AND OPERATING CONDITIONS

Cumulative Operating Time (hrs.)	Feed Pressure (psi)	Conversion (%)	Feed Conductivity (mhos/cm)	Temp. (°C)	Measured Productivity (gpd)	Corrected Productivity (gpd)
22	170	67	1400	26	1.90	2.25
46	180	67	800	23	1.90	2.35
105	130	72	825	27	1.78	2.28
130	185	60	550	56	1.93	2.42
160	185	63	300	27	1.68	2.21
225	160	80	600	27	1.53	2.30
328	170	66	400	23	1.51	2.23
386	170	80	320	23	1.51	2.23
456	170	69	120	26	1.32	2.19
485	180	63	470	24	1.66	2.18
617	205	80	600	23	1.51	2.23
674	170	80	620	26	1.51	2.18
675	200	86	180	28	1.68	1.98
692	160	69	420	27	1.52	2.18
693	195	80	950	23	1.78	2.35
738	175	67	80	27	1.40	2.06
800	160	66	600	25	1.51	2.13
809	200	84	1100	27	1.87	2.61
922	160	76	1250	32	1.76	2.47
967	200	77	3800	21	1.79	1.99
1056	195	76	3150	23	1.83	2.08
1061	200	77	4100	23	1.79	1.99
1120	200	50	17500	27	1.69	1.91
1130	195	73	7750	28	1.75	2.04



NaCl Tests - At various times during the four month operation, the RO system was shut down, flushed, and operated on a standard 1500 ppm NaCl solution with total recycle. The results of these periodic tests are given in Table 10. The flux is plotted as a function of operating time in Figure 18. The flux decline with time is very slight. In fact, a line of zero slope would fit the data points quite well. The loss of flux calculated by an extrapolation of the curve in Figure 18 is about 9% per year. Thus, from the NaCl tests, the loss of flux can be attributed primarily to compaction of the polyamide fiber. In any case, it can be concluded that the flux remains quite stable with operating time.

Rejection

Data Correction - The rejection of a membrane is defined by

$$r = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \qquad (3)$$

where:

r = Rejection usually expressed in %
C_f = Concentration of species in feed
C_p = Concentration of species in permeate.

The dependence of rejection on operating pressure and osmotic pressure can be derived by noting that the passage of salt through the membrane is given by:

$$J_s = K_s(\Delta C) = K_s(C_f - C_p) \qquad (4)$$

where:

J_s = Flux of solute
K_s = Constant characteristic of membrane
ΔC = Solute concentration difference across membrane.

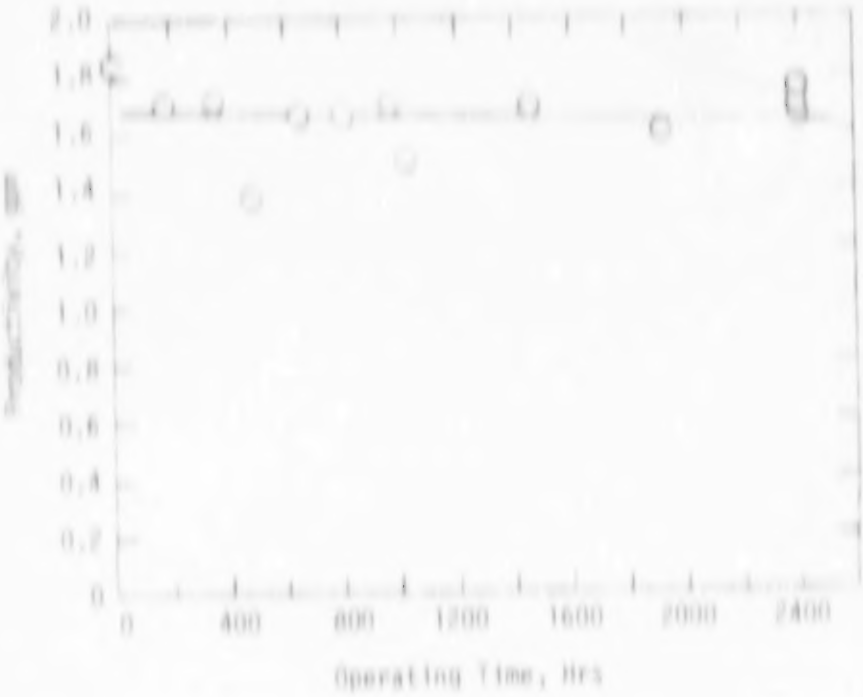


Figure 18. Corrected Productivity for Standard NaCl Solution vs. Operation Time (RFP Co.).

the concentration of solute in the permeate (C_p) is equal to the flux of solute (J_2) divided by the total flux of material ($J_1 + J_2$), or, since $J_2 \ll J_1$, equations (1), (3), and (4) combine to give:

$$r = \frac{1}{1 + \frac{K_2}{K_1 (\Delta P - \Delta \pi)}} \qquad (5)$$

Since both K_1 and K_2 have the same temperature dependence, the rejection is essentially independent of temperature.

Equation (5) indicates that as the feed concentration and conversion increase ($\Delta\pi$ increases), the rejection decreases.

The correction is not difficult to apply if the average feed concentration can be estimated and the average osmotic pressure calculated. However, for plating solutions the rejection does not follow the dependence on feed concentration given by equation (5). Figure 19 shows the rejection as a function of feed concentration for the Rochelle copper cyanide bath tested in the in-house pilot phase of the program [2, 3]. The rejection increases with increasing feed concentration up to a total dissolved solids concentration of about 5%. The ionic equilibria are more complex for plating solutions than for simple salts. In solution, cuprous ions and cyanide ions associate to form the following complexes:

$$Cu(CN)_2^-$$
$$Cu(CN)_3^{=}$$
$$Cu(CN)_4^{\equiv}$$

The degree to which the above complexes are formed depends on the solar concentration of the solution. As the solution becomes increasingly dilute the complexes tend to dissociate. Since rejection increases with ionic size and ionic charge, rejection can be expected to increase with increasing concentration until a point is reached where the formation of larger complexes no longer outweighs the effects on rejection of the increase in osmotic pressure (equation [5]).

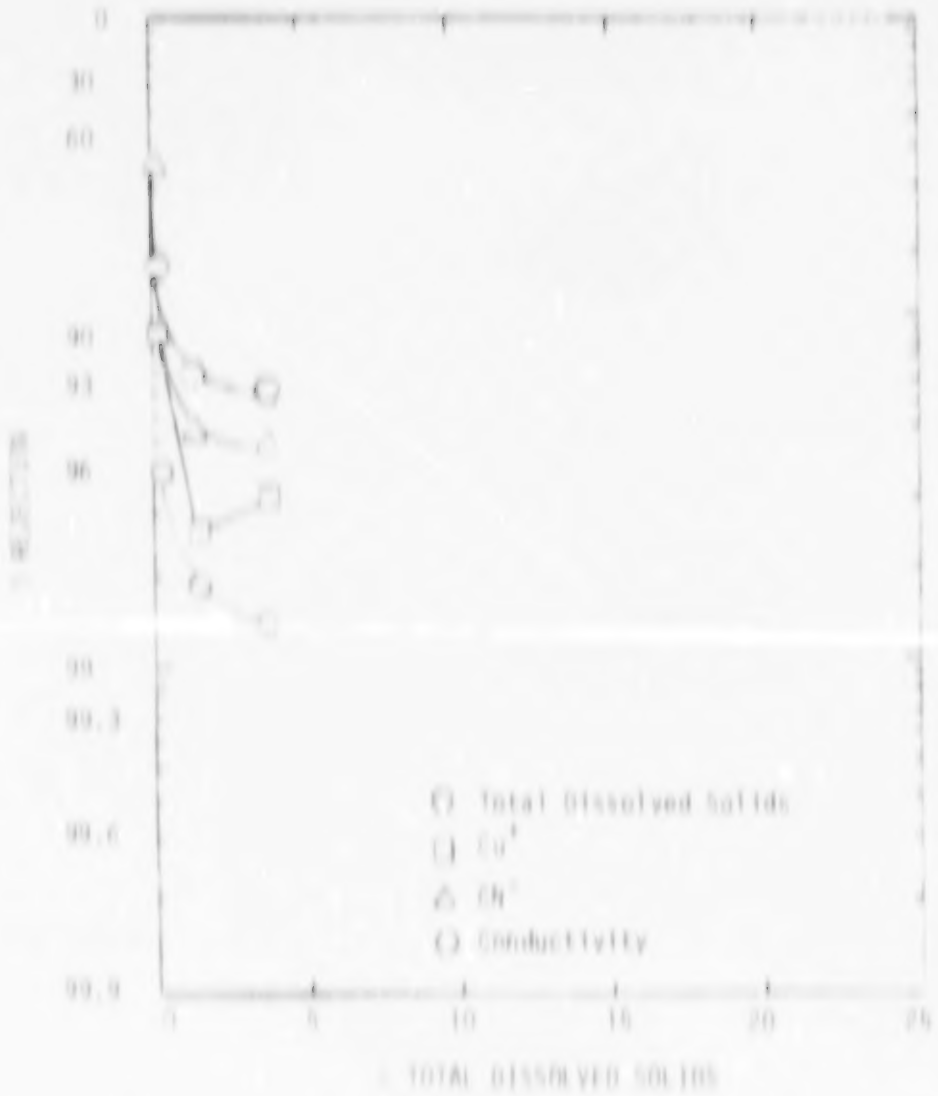


Figure 19. Rejections for Rochelle Copper Cyanide Rinse Waters.

Because of this unorthodox dependence of rejection on concentration, the data were not corrected for feed concentration and conversion.

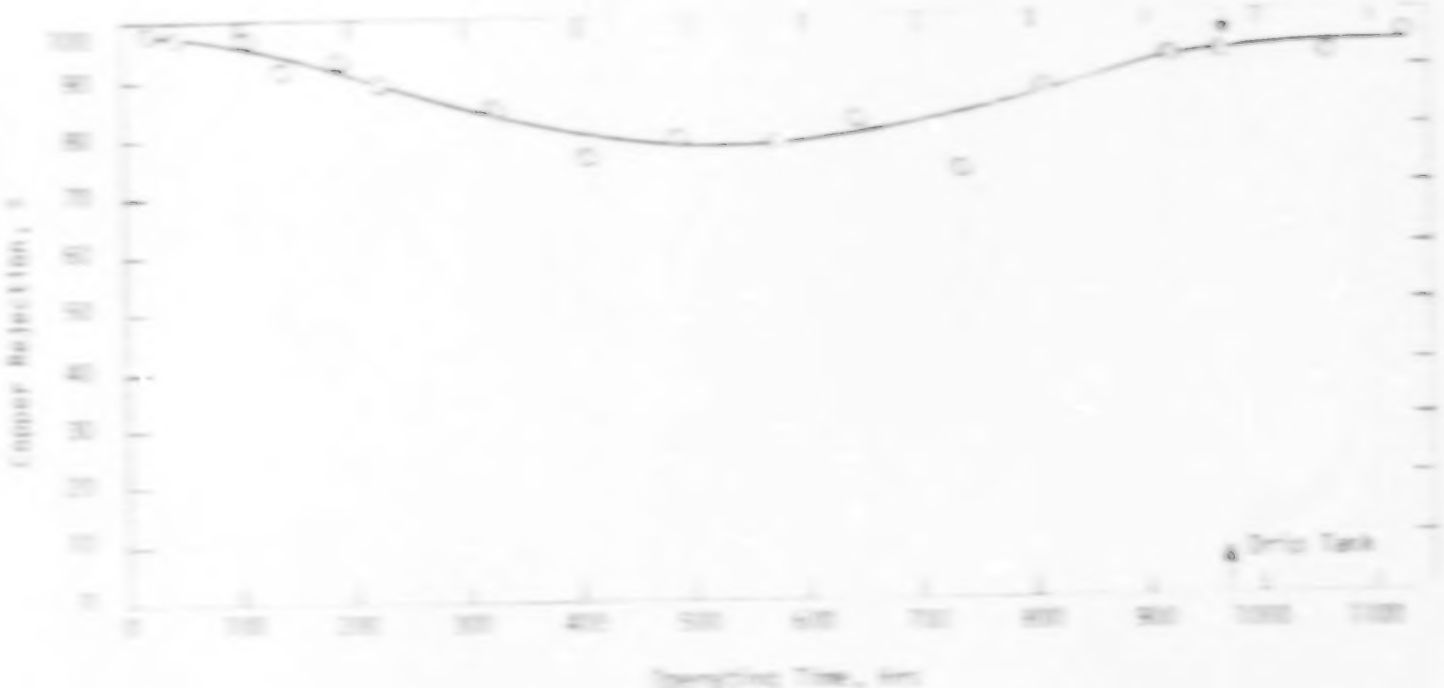
The correction curve given in the duPont Technical Information Manual was used to correct for the effect of operating pressure on rejection. This curve is consistent with equation (5) over the pressure range of interest for the great majority of the data. For very concentrated solutions, the duPont correction curve is inapplicable and equation (5) was used directly.

Dependence on Time : Conductivity rejections are given in Table 11 and Figure 20. The rejection decreased over the first 300 hours of operating time to a value of about 70% and then appeared to increase again although there is considerable scatter in the data. The scatter may be due, in part, to the dependence of rejection on feed concentration. The feed concentration could not be controlled at a set value, and the data were not corrected for variations in feed concentration. A drip tank was installed at 967 hours of operating time to continuously add bath to the rinse tank, simulating a continuous dragout. During this period the feed concentration was greater than the maximum feed concentration observed without the drip tank. The rejections between 967 and 1130 hours were better, on the average, than the rejections prior to the installation of the drip tank. This suggests that the rejection increases with increasing feed concentration which is contrary to the theory and typical behavior for simple salts.

Copper rejections are given in Table 12 and Figure 21. The variation in copper rejection with operating time is stellar to the variation of conductivity rejection shown in Figure 20. The copper rejection goes through a minimum of about 80% at 500 hours. During the drip tank operation the copper rejections were very good.

TABLE 12. COPPER REJECTIONS AS A FUNCTION OF OPERATING TIME AND OPERATING CONDITIONS

Cumulative Operating Time (hrs)	Feed Pressure (psi)	Conversion (%)	Copper Concentration (mg/l) Feed	Permeate	Concentrate	Rejection (%)	Corrected Rejection (%)
22	170	67	190	10	1250	95	98
46	190	67	120	7	770	94	97
105	135	72	140	11	740	92	97
138	165	90	50	11	380	78	91
186	165	83	90	15	50	83	93
225	160	90	60	23	530	71	89
326	170	88	40	15	230	62	86
403	170	85	12	7	65	42	76
467	205	88	70	27	400	61	79
535	200	86	48	20	190	58	78
648	195	86	76	27	560	65	82
736	175	87	83	51	310	38	73
809	200	94	136	35	675	74	87
922	190	76	134	23	580	83	92
967	200	77	425	60	2300	86	93
1067	200	77	510	67	2780	84	92
1130	195	73	460	54	2440	81	96



Similar behavior is also noted for the total solids rejections given in Table 13 and Figure 22.

The pH's of the feed, permeate, and concentrate were also measured and used to calculate the hydroxide ion rejections given in Table 14. In many cases negative rejections were obtained indicating that the rate of transport of OH^- through the membrane was faster than the rate of transport of water. The average rejection of OH^- calculated from the values of Table 14 is very nearly zero percent.

Free cyanide concentrations were measured only during the latter part of the field test. The concentrations and rejections (uncorrected) are given in Table 15.

Dependence on Concentration - The rejection of copper cyanide plating salts appeared to improve during the period that the drip tank was operated, suggesting a positive correlation between rejection and feed concentration. The corrected conductivity rejection is plotted against the conductivity of the feed in Figure 23. Although there is considerable scatter in the data, a positive correlation between rejection and feed concentration is obtained.

The relation between feed concentration and rejection was investigated directly. Feed solutions of various concentrations were prepared in an auxiliary feed tank by diluting a portion of the plating bath. The RO unit was operated in a total recycle mode on each feed solution and samples were analyzed for conductivity. Results are given in Table 16. A modified procedure was used to correct the data because of the high osmotic pressure of some samples. The correction procedure is given in Table 16. Both the uncorrected and corrected rejections show the same trend: an increase in rejection with increasing feed concentration. This follows the theory outlined previously, i.e., dissociation at low concentration to species which are poorly rejected.

NaCl Rejections - While the rejection of various plating salts is important in determining the extent to which plating chemicals can be recovered, it is difficult to determine the rejection stability from these data because of the dependence of rejection on feed concentration. The true measure of rejection stability of the membrane with operating time is obtained from the standardized NaCl tests. These rejections are given in Table 10 and are plotted in Figure 24 as a function of operating time. Only a moderate decline in rejection occurred over the 100 days of operating time: from 90% to 85%. This decrease is acceptable for certain plating applications as will be shown in Section VI.

It should be emphasized that the rejection decline for NaCl will be greater than for the plating chemicals. When the membrane rejection declines, the rejection declines most rapidly for species which are poorly rejected (small monovalent ions such as sodium and chloride). The decline in rejection is slower for species which are highly rejected (large multivalent ions such as copper cyanide complexes). Thus, the rejection decline for NaCl should give a conservative estimate of the rejection decline for copper cyanide plating salts.

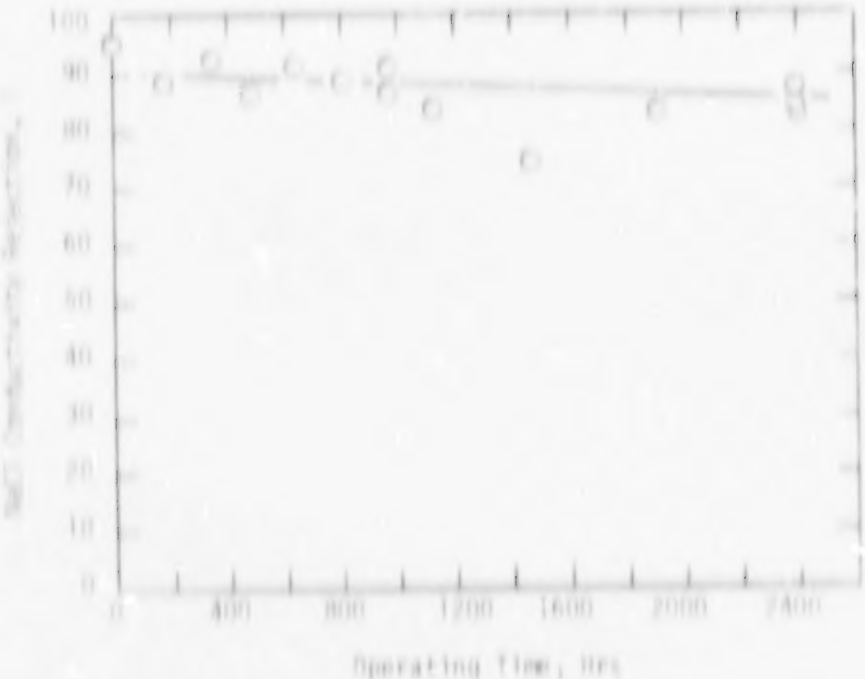


Figure 24. Corrected Rejections for Standard NaCl Solution vs. Operating Time (RFP 1a).

SECTION VI

DISCUSSION

WHYCO FIELD TEST

During field tests at Whyco Chromium Co., both the flux and rejection of the membrane declined within a period sufficiently short to make RO unattractive on the basis of membrane replacement costs. Based on the results of tests conducted on one of the Whyco modules, the reason for the decline in performance appears to be two-fold:

1. Chemical and physical degradation of the Reemay wrap material/flow-distributor; and
2. Chemical degradation of the skin of the hollow fiber membranes.

Laboratory tests conducted to identify the bad-actor constituent were successful in simulating the degradation of Reemay when massive doses of brightener were used. In the operation of a module, feed is distributed radially outward from a porous tube running down the axis of the module. In passing from the distributor tube to the outer radius of the module, the feed passes through concentric layers of hollow fine fibers, each layer separated by a thin paper-like material called Reemay. In a four-inch module, there are about 16 of these concentric fiber layers. The Reemay wrap material acts as a flow distributor by holding the fibers in position. Without this material, the feed solution would create channels through the fiber bundle.

The Reemay removed from the brightener-life-test module showed a regular pattern of destruction particularly in outer layers. The most severly damaged portions lined up to form a channel of low flow resistance from the central distributor tube to the outer radius.

The poor rejection performance observed during the latter part of the life test with brightener (Figure 15) was probably the result of poor flow distribution in the module. In pockets where the flow is very low, the con-

centration builds up because of the permeation of water through the fibers. In addition, when the flow is low the boundary layer is thicker, and the concentration at the membrane surface builds up relative to the bulk concentration (concentration polarization). In regions of very low flow the osmotic pressure at the membrane surface can approach the operating pressure of the module. Since the salt flux through the membrane is directly proportional to the concentration of salt at the membrane surface, poor flow distribution leads to high salt passage or low rejection. Thus the degradation of the Beesay results in low overall rejections even though the hollow fiber membranes themselves remain intact.

While deterioration of Beesay was simulated during the laboratory tests, no significant deterioration of the hollow fiber membranes was observed during these tests even in the presence of massive doses of brightener. This is particularly evident from the high and stable rejections observed during mini-permeator tests. Since mini-permeators do not contain Beesay and are not limited by poor flow distribution, they give a direct indication of membrane performance as opposed to module performance. In addition, dye tests on some of the fibers from one of the laboratory test modules indicated that membrane attack was not the major reason for the decline in module performance when exposed to massive doses of brightener. It is concluded that the polyamide membrane is highly resistant to the brightener and to the other major constituents of the bath.

Since chemical degradation of the membrane fiber could not be simulated in the laboratory tests, it is concluded that the constituent responsible for chemically attacking the membranes at Whyco is not a major bath constituent. At present, its identity has not been determined.

It is evident that a wrap material/flow distributor is essential to the proper operation of a duPont hollow fiber permeator. However, it appears that Beesay is not sufficiently resistant for copper cyanide applications. Contacts with the manufacturer have indicated that it would be possible to substitute a more chemically resistant material for Beesay on a special-order basis. It would appear that application of hollow-fiber permeators to cyanide baths

should be based on such modules.

The field test at Whyco illustrates the danger of extrapolating laboratory results to actual applications. In terms of module performance the field test was unsuccessful even though laboratory life tests were very promising. It is recommended that field tests be conducted on the specific waste stream to be treated prior to the purchase of RO equipment. Meaningful field tests can be conducted with a relatively low level of effort. The system can consist of little more than a cartridge filter, a pump, and a half-size module operated on the overflow from the first rinse tank. It is not necessary to return either the concentrate or permeate to the plating operation. A sodium chloride flux and rejection test before and after three months of field operation should give a good indication of membrane stability.

Alternatively, it is recommended that a performance guarantee be obtained from the supplier of membrane equipment. This guarantee will likely require the supplier to conduct field tests on the bath unless previous experience indicates the application is a highly successful one.

NEW ENGLAND PLATING FIELD TEST

The results of the field test at New England Plating appear much more favorable. The flux stability, as determined by the standard Hall performance tests, was quite good. Within the scatter of the data, fouling was not significant. The rejection stability, as determined by the standard Hall performance tests, was much better than at Whyco, but a moderate decline was observed. This decline may again be related to degradation of the Beemay wrap material.

The economics for closed-loop RO treatment of this particular plating bath can be estimated from the data obtained during the field test. A more generalized presentation of economics is given in the following section.

The present rinsing system at New England Plating consists of two tanks operated countercurrently; no chemicals are recovered by this system. The maximum allowable concentration in the final rinse is 100 mg/l of total solids

or about 4×10^{-4} times the bath concentration. The RO system would be designed to operate as shown in Figure 25. A single half-size 6-9 module would be operated at 75% conversion to given 2.0 gpm of permeate. The capital cost for such a system would be about $8,500.

Figure 26 shows the second rinse concentration as a function of rejection. The rejection can decrease to about 65% before the concentration limit is exceeded. For design purposes it is assumed that the decline in rejection follows that measured for NaCl. Thus, by extrapolation of Figure 24, the life of the module is 500 days.

The breakdown of the operating cost is shown in Table 17. The total operating cost for the RO system is $2.94 per day.

The operating cost of the RO system can be offset by credits resulting from closed-loop recovery. The major credits result from recovery of plating chemicals and from the savings in destruction chemicals previously used to oxidize cyanide and precipitate copper. The credit resulting from the reduction in water usage is minor in comparison. Table 18 gives the breakdown of credits for New England Plating. Based on one operating shift per day, the total credits amount to $2.65 per day.

The operating cost is almost entirely offset by the credits resulting from closed loop operation; however, for this particular plating line the credits are insufficient (in relation to the operating cost) to make the capital investment attractive on a purely economic basis. Therefore, an RO system would be recommended for New England Plating only if complete closed-loop treatment using the present two-stage rinse were required. Since this particular plating line is a manual rack operation, closed-loop treatment could be achieved by adding more countercurrent rinse stages. Theoretically, a three-stage rinse would give a final rinse purity very close to the specified concentration.

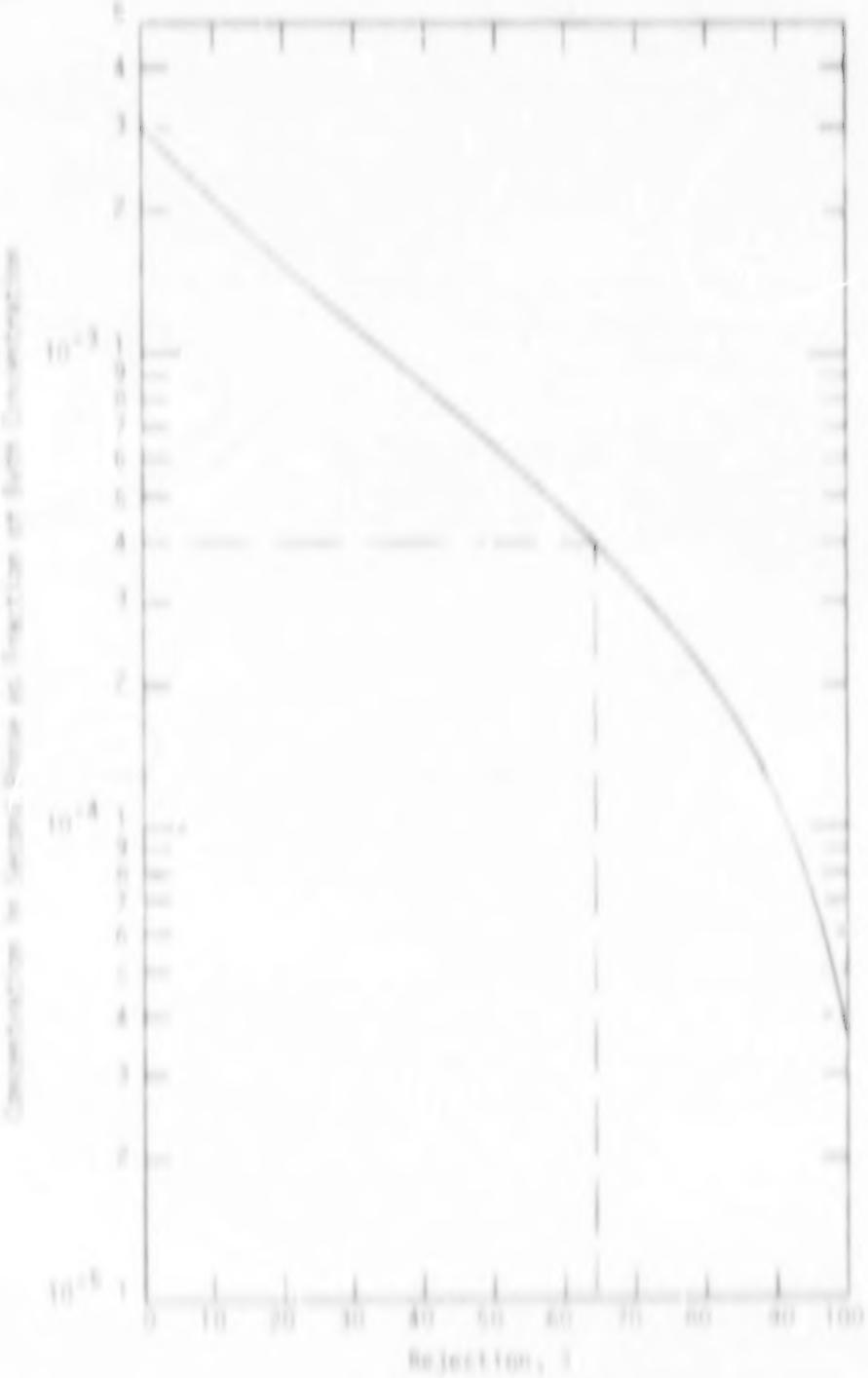


Figure 26. Concentration in Second Rinse vs. Rejection for Half-Size B-9 Module Operated at 75% Conversion.

TABLE 17. BREAK-DOWN OF OPERATING COSTS FOR NEW ENGLAND PLATING

1. Power (at $0.036/kwh)

   Motor power requirement is for high pressure pump
   (flow rate = 2.67 gpm; ΔP = 400 psi; motor/pump efficiency = 50%)

   Power consumed = $\frac{(2.67)(400)}{(1715)(.50)}$ = 1.25 hp

   Daily cost = (1.25)(.745)(8)(0.036) = $0.27 per day

2. Module Replacement ($720 each); 500 day life

   Daily cost = $\frac{\$720}{500}$ = $1.44 per day

3. Maintenance (5% of capital investment per year)

   Daily cost = $\frac{(.05)(10,500)}{365}$ = $1.16 per day

4. Deionized Water

   (based on cost of $2.00 per 1000 gal from central deionizer
   which uses RO for water pritreatment)

   Daily cost = (.023)(1440)($.002) = $0.07 per day

TOTAL OPERATING COST = $2.94 ($1.02 per 1000 gal permeate)

TABLE 18. CREDITS REALIZED FOR RO OPERATION AT NEW ENGLAND PLATING

1. Chemical Credits

Bath composition and unit cost of chemicals:

Constituent	Concentration	Unit Cost
CuCN	8.5 oz/gal	$1.87/lb
(Cu as metal)	(6.0 oz/gal)	
NaCN	16.0 oz/gal	$0.61/lb
Rochelle Soln	6% Vol	$3.55/gal
Brightener	2000 ppm Vol	$5.20/gal

Value of plating solution = $1.83/gal

Minimum recovery of RO system = $\frac{1 - 4 \times 10^{-4}}{1}$ = 99.96%

Daily Savings per shift = $\frac{(.9996)(.0013)(1440)(\$1.83)}{1}$ = $1.14 per day

2. Water and Sewer Credits

Assume water and sewer costs at $0.50/1000 gal

Present water requirements for two-stage countercurrent rinse and final rinse concentration of 4×10^{-4} times bath concentration = 62 gpd (one shift per day)

Daily Savings = (62)($0.0005) = $0.03 per day (one shift per day)

3. Chemical Treatment Credits

Total cyanide concentration in bath = 8.9 oz/gal

Daily dragout = $\frac{(.0013)(1440)(8.9)}{(2)(16)}$ = 0.35 lb/day

Requirements for chemical destruction: Caustic = 1.0 lb/lb CN
Chlorine = 8.0 lb/lb CN

Cost for chemicals as used: Caustic = $0.22/lb NaOH from 50% soln
Chlorine = $0.50/lb Cl_2 from 15% NaOCl soln

Treatment cost = $4.22/lb CN

Daily Savings = (0.35)($4.22) = $1.48 per day

TOTAL CREDITS = $2.65 per day

GENERAL ECONOMIC PROJECTIONS

Care must be exercised in comparing the results from these two field tests and in extrapolating the results observed at New England Plating to other plating operations. The dragout at New England Plating was very small, and, compared to Whyco, a much longer operating time was required to give the membranes an equivalent exposure to plating chemicals. In addition, the ratio of evaporation to dragout at New England Plating was about 18 compared to about 10 at Whyco. Therefore, the concentrate returned to bath at Whyco was more concentrated. If the deterioration in module performance is related to the concentration of plating chemicals, a more rapid decline would be expected as the evaporation-to-dragout ratio decreases. Since it is impossible on the basis of present information to accurately extrapolate the life test data from one plating bath to another, it is recommended that a life test be conducted on the particular bath to be treated.

The capital cost for a closed-loop RO recovery system depends primarily on the size of the system in terms of the gallons of permeate per day that it can produce. Beyond this rather broad generalization, there are many factors which can significantly affect the capital cost but are often related in a complex way to the specific requirements for a particular installation. For example, the flux has a direct influence on the amount of membrane surface area required to achieve a given system output (in gallons of permeate per day). As the flux declines, the required number of membrane modules increases, and the capital cost increases.

The flux is determined, in part, by the intrinsic permeability of the membrane to water, the extent of compaction and fouling, the conversion at which the module is operated, and the degree to which the rinse waters must be concentrated. The degree of concentration depends on the ratio of bath evaporation to dragout which can vary widely from application to application. For baths with a low ratio of evaporation to dragout, the concentrate returned to bath must be highly concentrated resulting in a low flux. For these baths it may be more efficient to <u>partially</u> concentrate the rinse water with RO (to a concentration at which the flux becomes uneconomically low) and then

use an auxiliary evaporator to reduce the volume of the RO concentrate to be returned to the bath.

The capital cost of an RO system can also be affected by membrane rejection. If the rejection is too low to meet the platers' specification for the final rinse purity, additional purification will be required. The permeate from the RO system could be treated with a second RO system or with ion exchange. This would add significantly to both the capital and operating costs.

Nevertheless, approximate capital costs are shown as a function of system capacity in Figure 27. These capital costs are based on the rated productivity of 8-9 modules as determined with a 1500 ppm NaCl solution at 400 psi, 77°F, and 75% conversion. Also shown in Figure 27 is the capital cost for membranes alone. This curve can be used to estimate the additional capital cost for applications where the average productivity is lower than the rated productivity. The cost for membranes, based on the rated capacity, varies from about 10% to 25% of the total capital cost for the range of capacities covered by Figure 27.

Typical operating costs as a function of system capacity are shown in Figure 28. These costs are based on the same assumptions as given in Table 17, but they do not include the cost for deionized make-up water which must be based on the cost and usage for each particular application. In addition, these operating costs are based on the rated productivities of the modules. The operating cost given in Table 17 for New England Plating is somewhat lower than the cost indicated in Figure 28. This is due to the high productivity for this application which allows a half-size rather than a full-size module to be used. For applications where the average productivity is below the rated productivity, the operating cost will be higher than shown in Figure 28 since more membrane modules must be replaced.

It should be emphasized that these costs are only approximate. For more accurate costs, quotes should be obtained for the specific plating bath to be treated from manufacturers of membrane equipment.

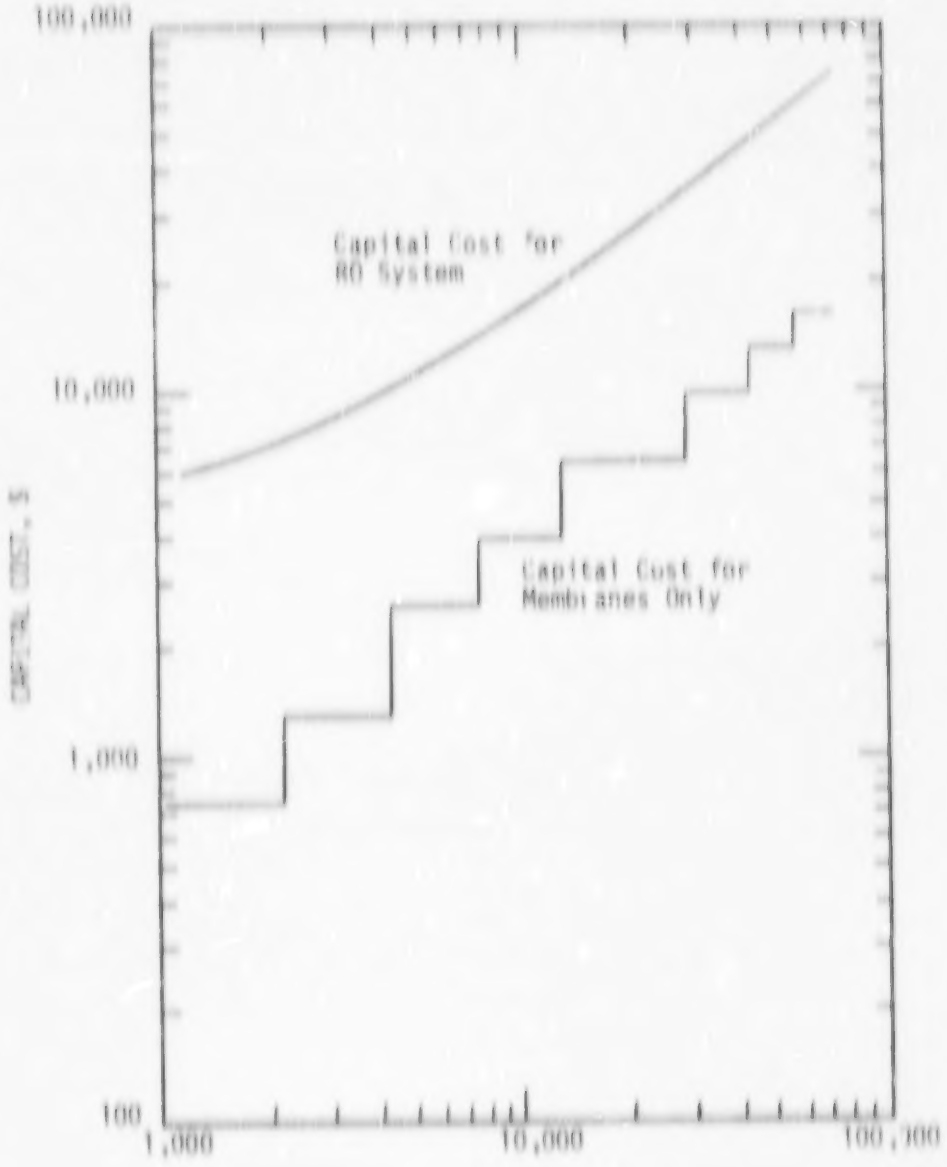


Figure 27. Typical Capital Costs for RO Systems.

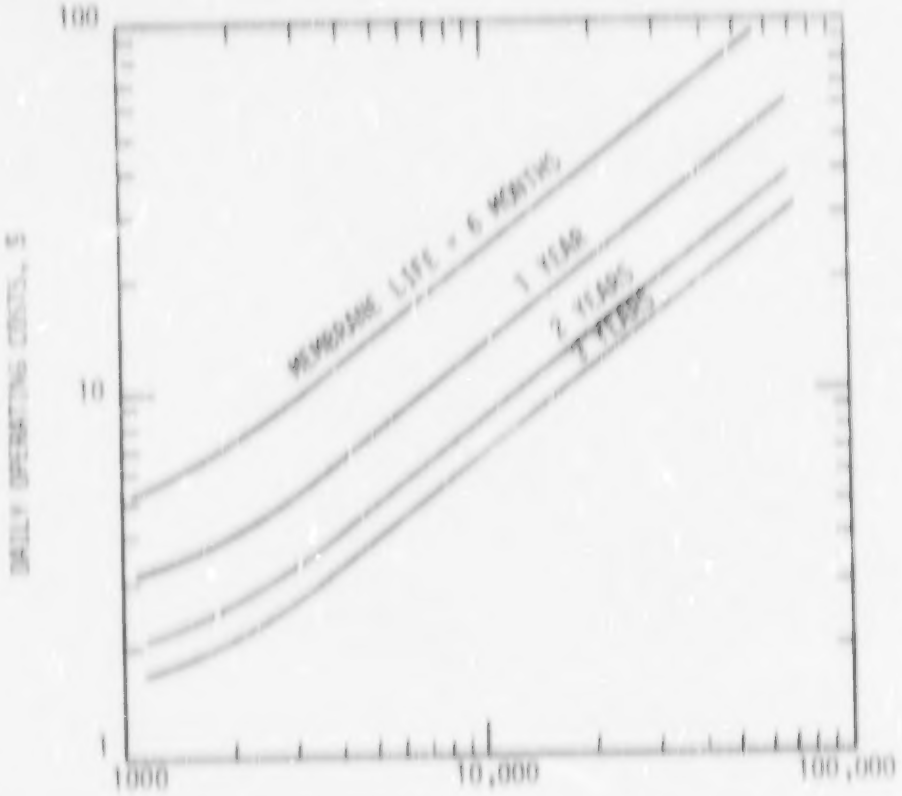


Figure 28. Typical operating costs for RO systems as a function of capacity and membrane life. (Does not include cost of DI make-up water.)

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